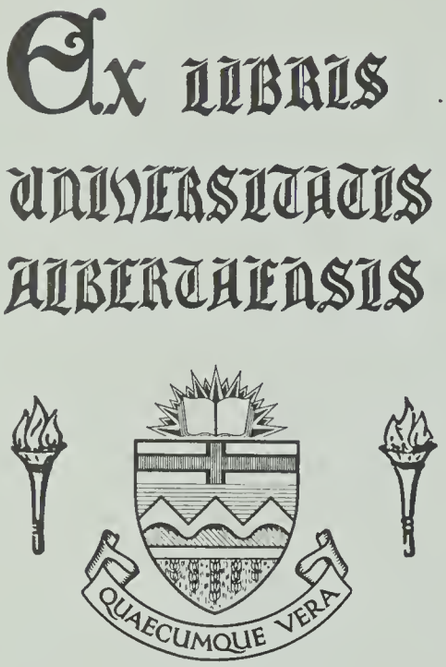

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SOME STUDIES OF THE CHEMISTRY OF CYCLOPROPENONES

by

© THOMAS W. MALONEY

A THESIS

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EDMONTON, ALBERTA

FALL, 1969

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled:

SOME STUDIES OF THE CHEMISTRY OF CYCLOPROPENONES

submitted by THOMAS W. MALONEY, in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The chemistry of cyclopropenones has been investigated with particular emphasis on the behaviour of these compounds toward nucleophiles and certain 1,3-dipoles derived from substituted aziridines. These reactions have been shown to fall into two categories. Nucleophilic attack or 1,3-dipolar addition can occur either at the carbon-oxygen bond or at the carbon-carbon double bond of the cyclopropenone system.

These studies have provided synthetic routes to novel pyrrole derivatives, substituted 4-oxazolines and derivatives of furan. The research was concluded with a study of the chemistry of diphenylcyclopropenethione including its reactions with oxidising agents and enamines.

ACKNOWLEDGEMENTS

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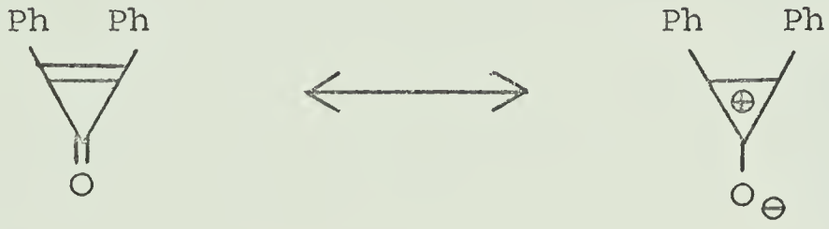
I. INTRODUCTION

Before their isolation, cyclopropenylium cations were predicted to be stable by theoretical considerations employed by Roberts, Streitweiser and Regan.[1] Later Roberts and Manatt calculated a large delocalisation energy for diphenylcyclopropenone using Hückel Molecular Orbital Theory.[2] This delocalisation can be represented as follows:-

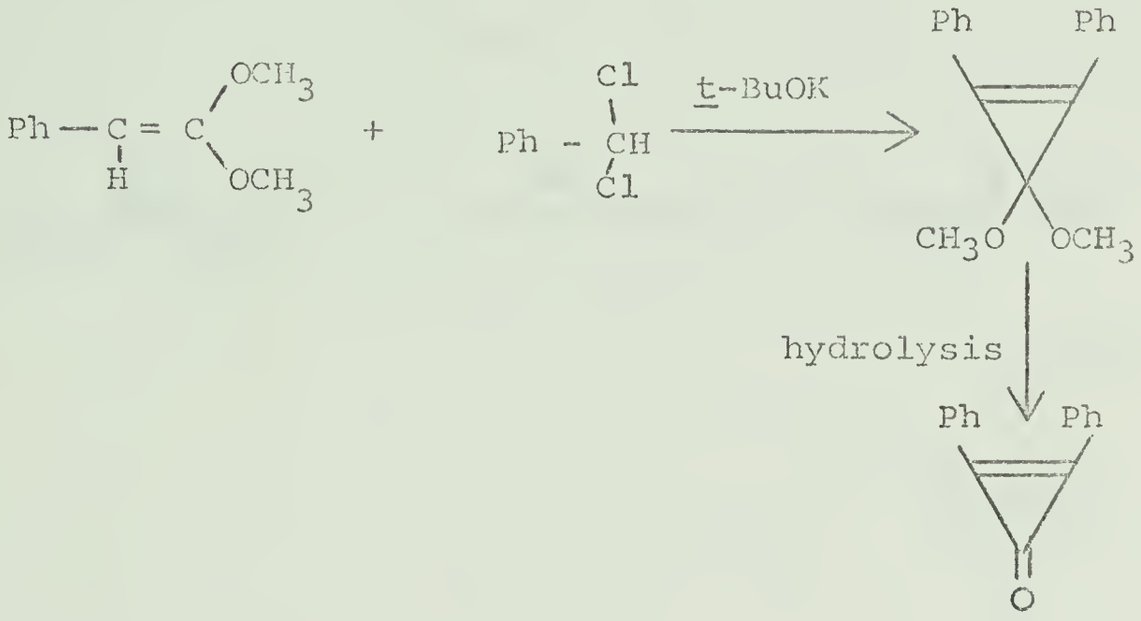


and was predicted to be sufficient to overcome the considerable strain in the molecule.

The cyclopropenyl cation represents the simplest aromatic systen according to Hückel's $(4n + 2)\pi$ rule where $n = 0$[3,4] and it is analogous to the tropone system which is written as follows:-

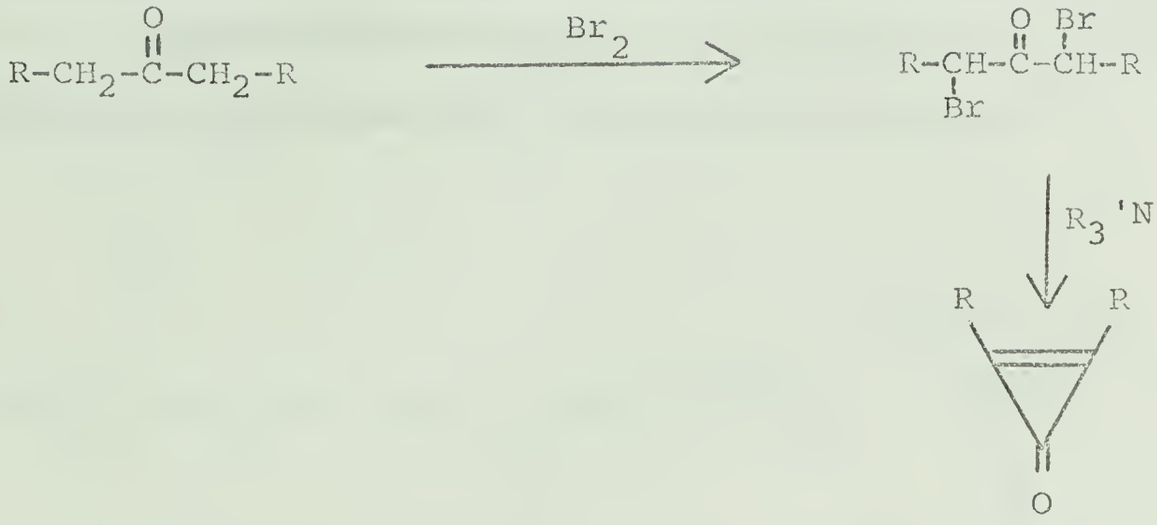
In 1959,two workers reported independent syntheses of diphenylcyclopropenone. Breslow and co-workers prepared diphenylcyclopropenone dimethyl acetal,by reaction of 1,1-dimethoxy-2-phenylethylene with benzylidene dichloride in the presence of potassium

t-butoxide.[5] Hydrolysis of the resultant dimethyl acetal derivative afforded diphenylcyclopropenone.

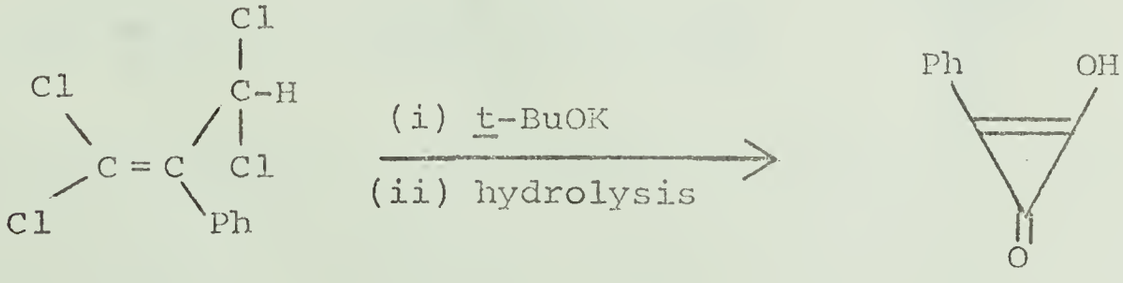


Vol'pin and his co-workers reported a synthesis of the same compound by a related reaction.[6] Addition of "dibromocarbene" to diphenylacetylene followed by hydrolysis resulted in the formation of diphenylcyclopropenone.

Since these preliminary publications, Breslow and co-workers have shown that both diphenylcyclopropenone and dialkyl substituted cyclopropenones can be prepared by a modified Favorskii rearrangement, in which an α,α'-dibromo-ketone is treated with a tertiary amine.[7,8] This method has provided novel routes to dipropylcyclopropenone, dibutylcyclo-propenone, cyclopheptenocyclopropenone and cycloundecenocyclo-propenone. This method also represents the most convenient preparation of diphenylcyclopropenone.

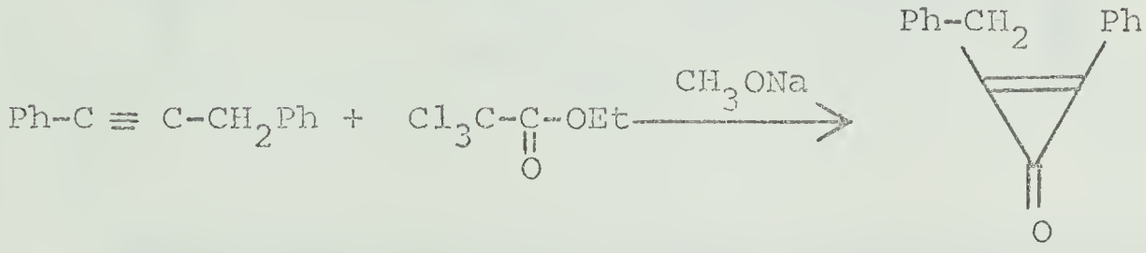


The original method involving "carbene" addition to activated sites of unsaturation appears to be the most general route to cyclopropenones and their derivatives. By using a modification of this technique, Farnum and Thurston have reported a preparation of 2-hydroxy-3-phenylcyclopropenone by using 1,1-dichloro-2-(dichloromethyl)-2-phenylethylene.[9]

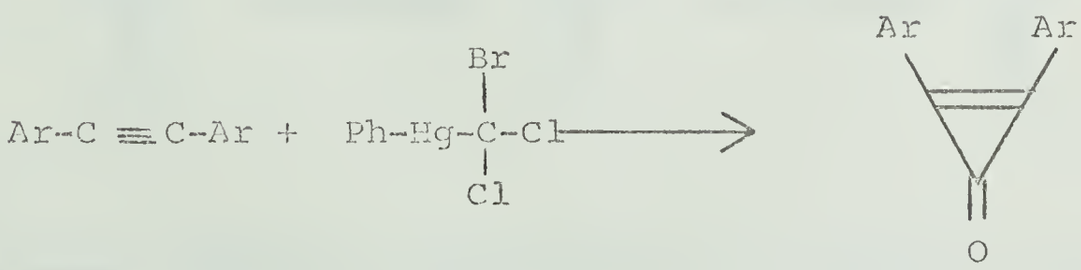


2-Hydroxy-3-phenylcyclopropenone is a strong acid, and osmometric measurements have shown that this compound exists as an associate dimer in dioxan solution, although its sodium salt is monomeric in aqueous solution.

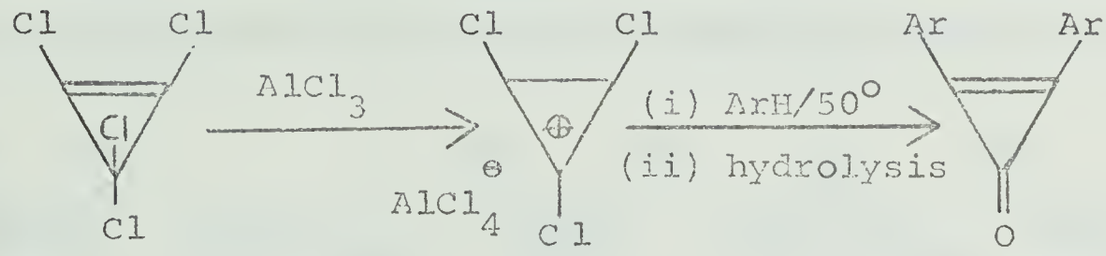
Kostikov and D'yakonov have prepared 2-benzyl-3-phenylcyclopropenone from benzylphenylacetylene.[10]



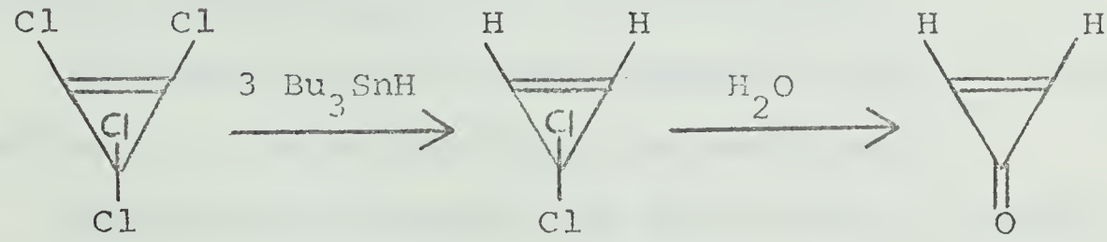
Related to these methods, is a procedure outlined recently by Seyferth and Damrauer, which describes a general method for the preparation of diarylcyclopropenones, by reaction of diarylacetylenes with phenyl bromodichloromethyl mercury.[11]



Tobey and West have proposed a general method for the preparation of diarylcyclopropenones, by a modified Friedel-Crafts reaction using the trichlorocyclopropenyl cation.[12] This method, however, seems useful only for highly activated aromatic hydrocarbons.



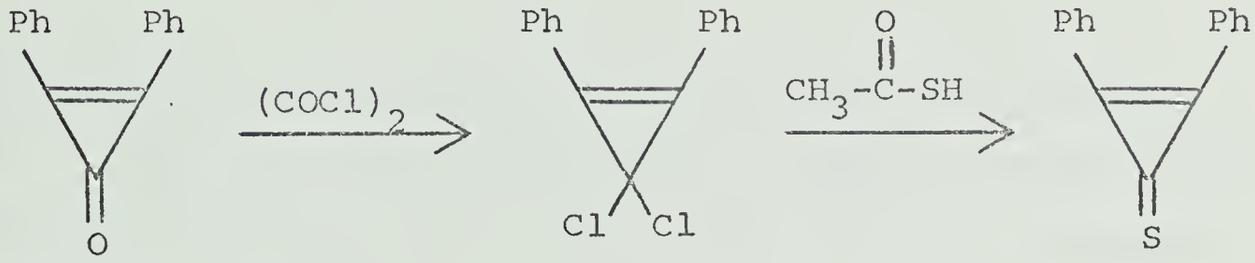
Breslow and Ryan have utilised tetrachlorocyclopropene to synthesise the parent cyclopropenone.[13] Reduction of tetrachlorocyclopropene with tributyl stannic hydride afforded 1,1-dichlorocyclopropene which was hydrolysed in water to yield cyclopropenone.



In aqueous solution, cyclopropenone is reported to have a half-life of greater than seven days, and although it cannot be distilled in the pure state without decomposition, this compound can be extracted from aqueous solution by salting out,

followed by extraction in either methylene dichloride or 1,2-dichloroethane.[13]

In 1965, Eicher and Frenzel reported a synthesis of the sulfur analogue of diphenylcyclopropenone.[14] When diphenylcyclopropenone was treated with oxalyl chloride, 1,1-dichloro-2,3-diphenylcyclopropene resulted, which, when treated with thioacetic acid gave diphenylcyclopropenethione.

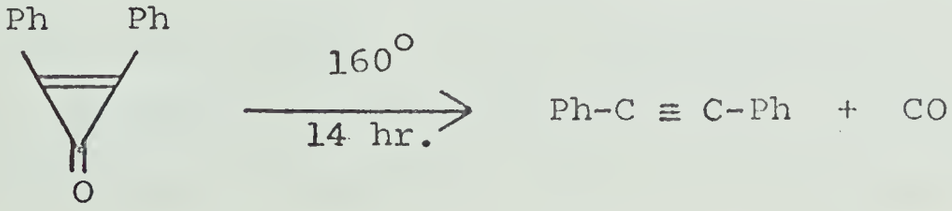


Tobey and West have shown that thionyl chloride can be used equally as well as oxalyl chloride in the conversion of diphenylcyclopropenone to 1,1-dichloro-2,3-diphenylcyclopropene.[12]

1. Chemical Reactions of the Cyclopropenones

The reactions of the cyclopropenones can be broadly classified into decarbonylations and additions.

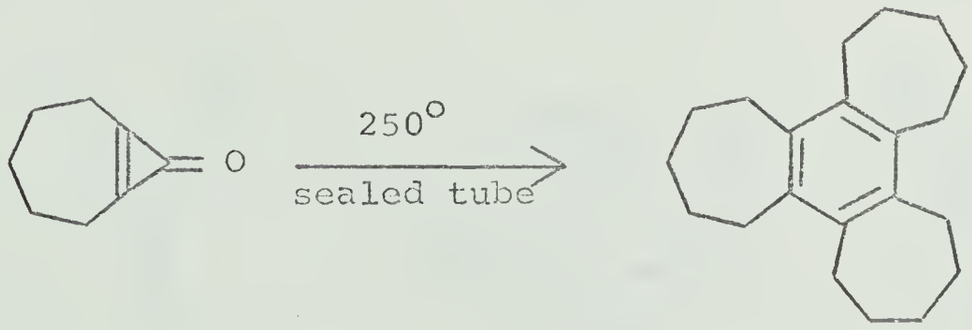
Diphenylcyclopropenone has been shown to undergo decarbonylation when heated at temperatures in the region of 160°, to yield diphenylacetylene in good yield.[7]



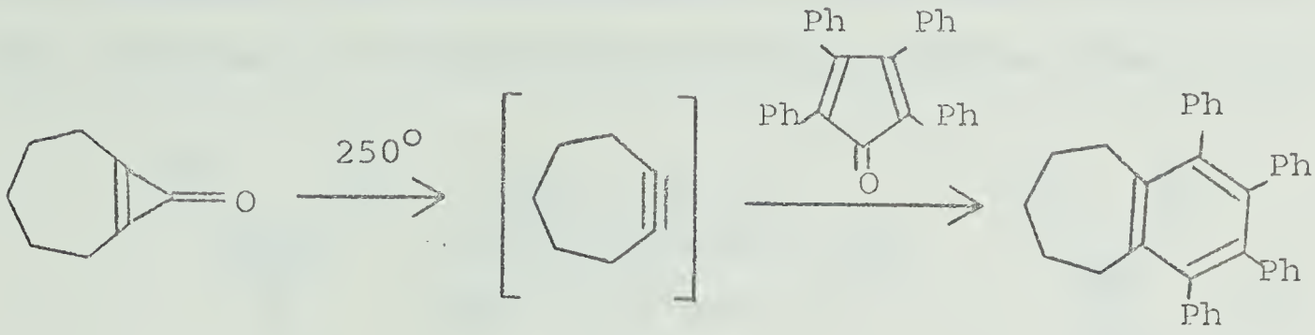
When heated at temperatures of 140-150°, diphenylcyclopropenone is reported to form a dimer whose structure has been tentatively assigned on the basis of spectroscopic evidence.[7]

This dimer does not yield diphenylacetylene when heated to 160°,[7] and it was also formed when a toluene solution of diphenylcyclopropenone was heated under reflux for prolonged periods of time.[15]

Breslow and co-workers have also shown that the decarbonylation of cycloheptenocyclopropenone results in the formation of triscycloheptenobenzene.[8]

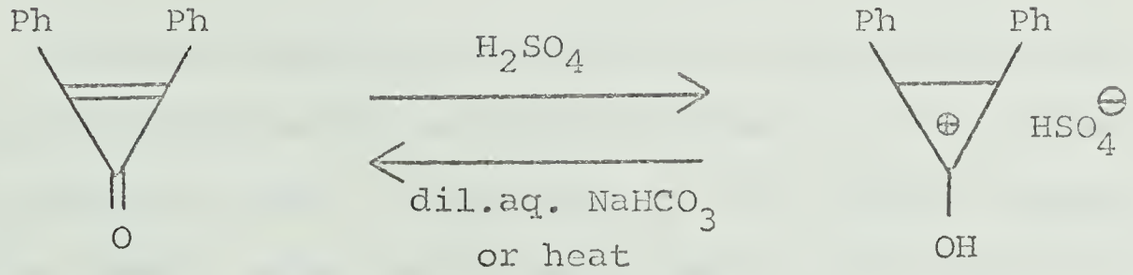


This reaction is thought to proceed through cycloheptyne, and evidence for this intermediate has been provided by these workers who have carried out the decarbonylation in the presence of tetraphenylcyclopentadienone when 1,2-cycloheptene-3,4,5,6-tetraphenylbenzene was given in 23% yield.[8]



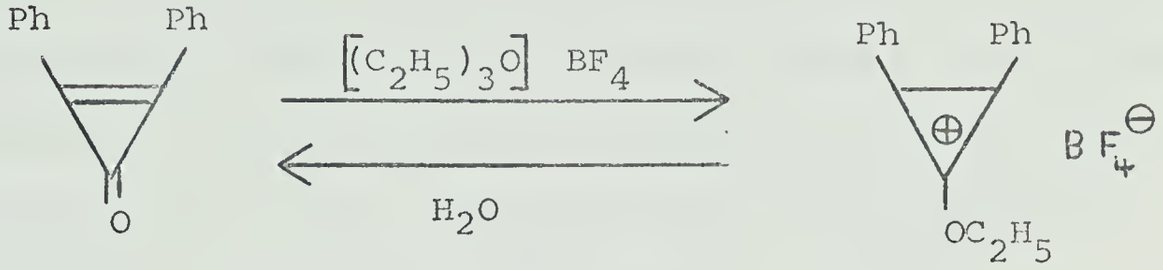
Addition reactions of the cyclopropenones can be further classified into two sub-groups, those in which the reactant adds to the C=O bond, and those in which the reactant adds to the C=C double bond of the cyclopropenone system.[16]

Cyclopropenones are basic and this property is readily illustrated by their reactions with strong acids to form salts, which in certain instances can be isolated as crystalline solids. For example, diphenylcyclopropenone reacts with sulfuric acid to give a bisulfate salt as a crystalline solid.[7]

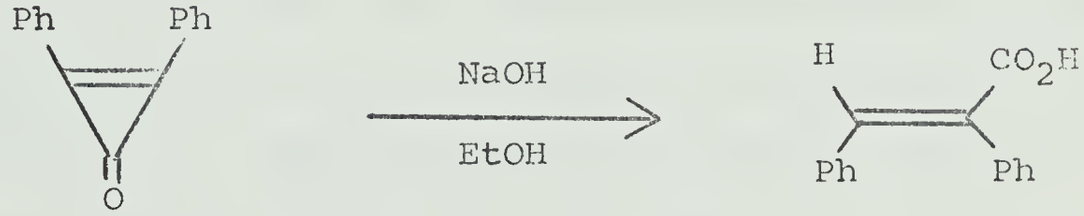


Salts of this type are readily decomposed by reaction with weak base and Breslow and co-workers have utilised this property of cyclopropenones in their separation and purification.[7] These workers have also shown that the reaction of diphenyl-

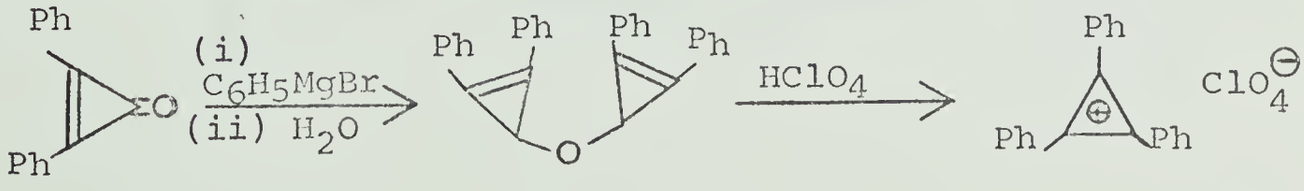
cyclopropenone with triethyloxonium fluoroborate results in the formation of ethoxydiphenylcyclopropenylium fluoroborate.[7]



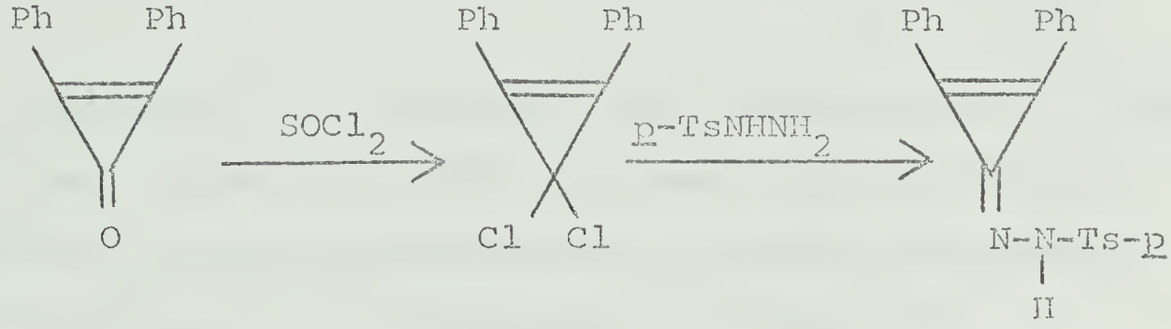
Cyclopropenones undergo hydrolysis in ethanolic sodium hydroxide solution; for example, diphenylcyclopropenone is rapidly hydrolysed to yield cis—α-phenylcinnamic acid.[7] The reaction is thought to proceed initially via a nucleophilic attack of hydroxide ion at the carbon atom of the carbonyl group.[16]



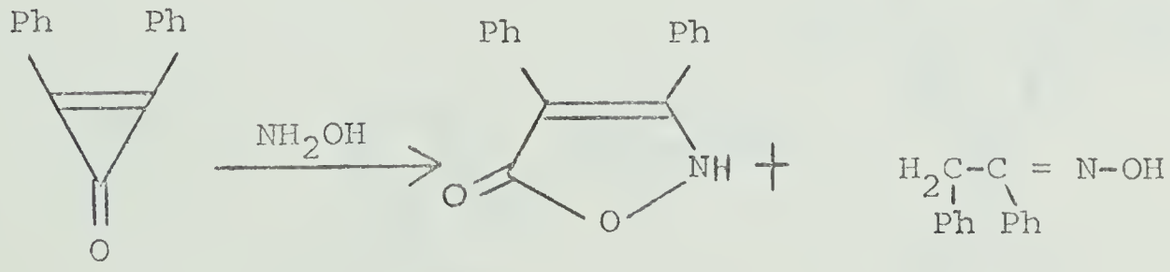
Grignard reagents also have been reported to react with cyclopropenones via an initial attack at the carbon atom of the carbonyl group. Hydrolysis of the Grignard complex yields a dimeric ether which when treated with strong acid yields the triphenylcyclopropenyl cation.[7]



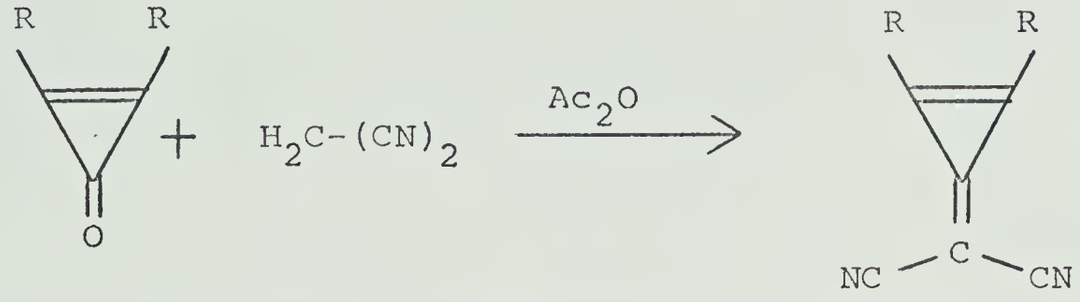
Simple carbonyl derivatives are not easily formed from cyclopropenones, and conflicting results concerning these derivatives are reported. For example Vol'pin and co-workers have reported that diphenylcyclopropenone forms a 2,4-dinitrophenylhydrazone[6] while Breslow and co-workers were not able to duplicate this result.[7] The p-toluenesulfonylhydrazone of diphenylcyclopropenone can be prepared, but only by an indirect method.[16]



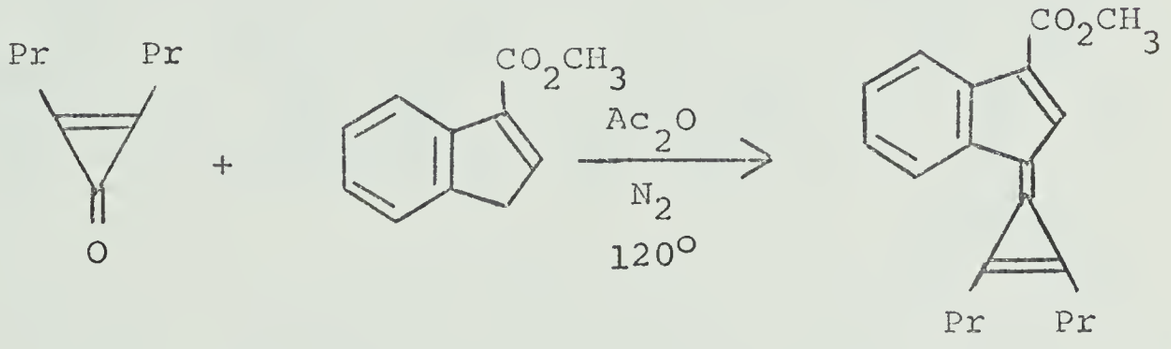
Breslow has shown that diphenylcyclopropenone reacts with hydroxylamine to yield 3,4-diphenylisoxazolone and desoxybenzoin oxime.[7] These products, he reports, are difficult to explain mechanistically, but he assumes that the first step involves a 1,2 or a 1,4 addition of hydroxylamine to the carbon-carbon double bond of the cyclopropenone system.[7]

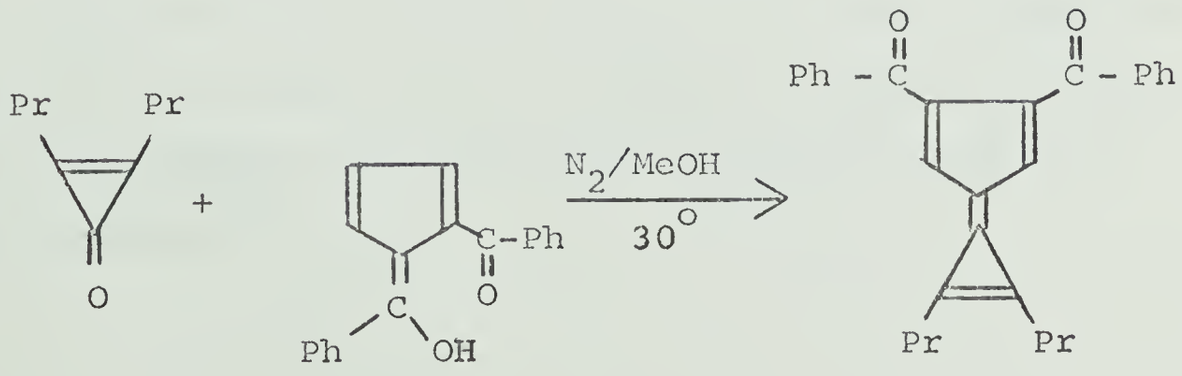


Bergmann, Agranat, Kende and Izzo have demonstrated that malononitrile can be condensed with the carbonyl group of the cyclopropenone system to yield derivatives of methylenecyclopropene.[17,18]

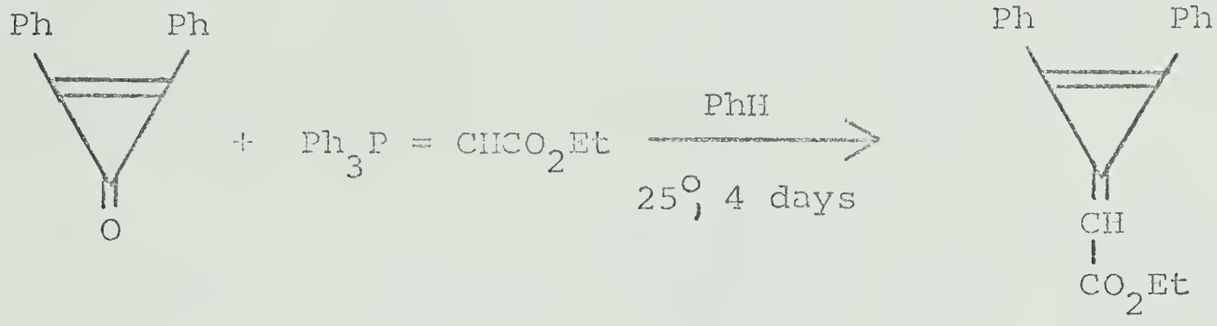


Related to this reaction with malononitrile, are reports that derivatives of the calicene system have been synthesised using cyclopropenones as starting materials. These reactions can be summarized as follows:-[19]

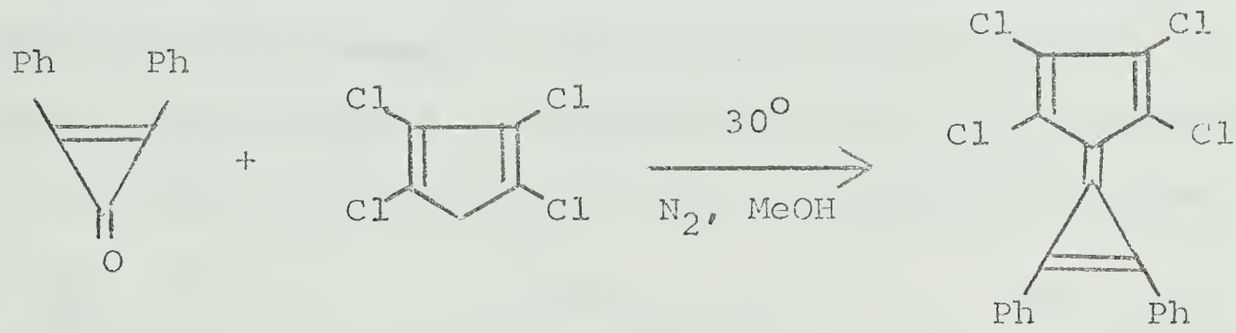




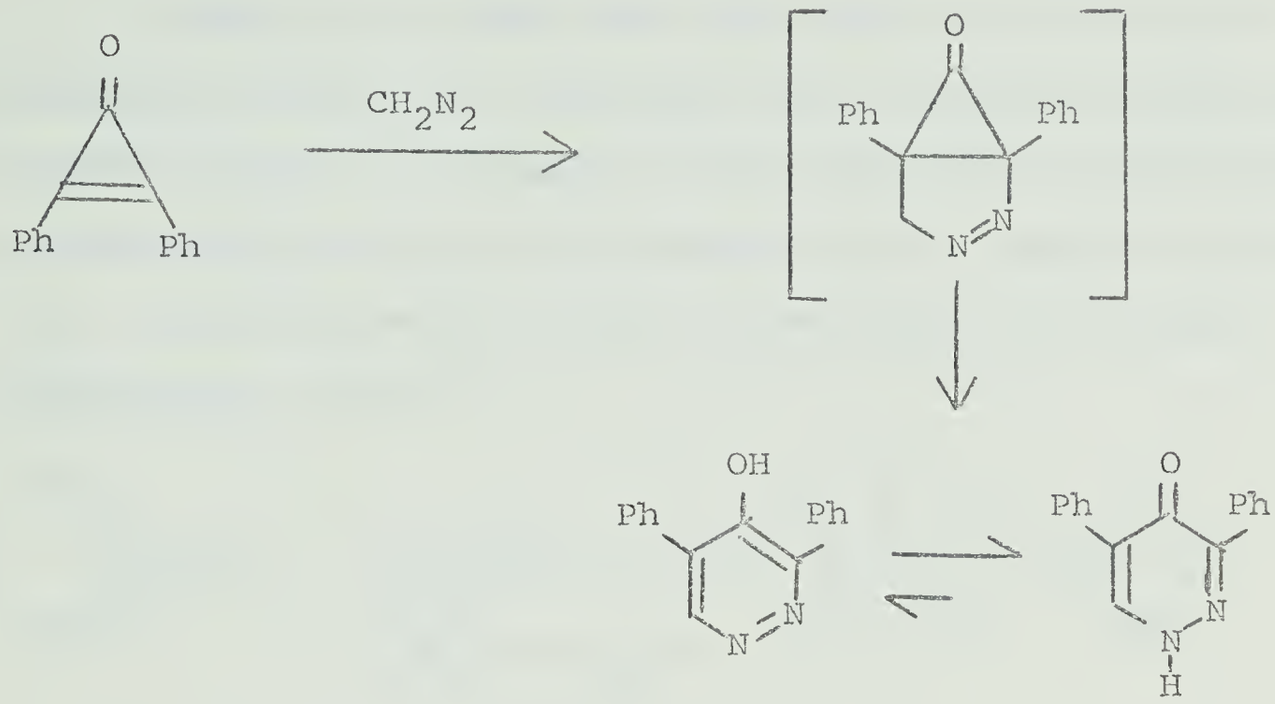
The Wittig reaction of carboethoxymethylenetriphenylphosphorane with diphenylcyclopropenone yields 1,2-diphenyl-4-carboethoxymethylenecyclopropene.[20]



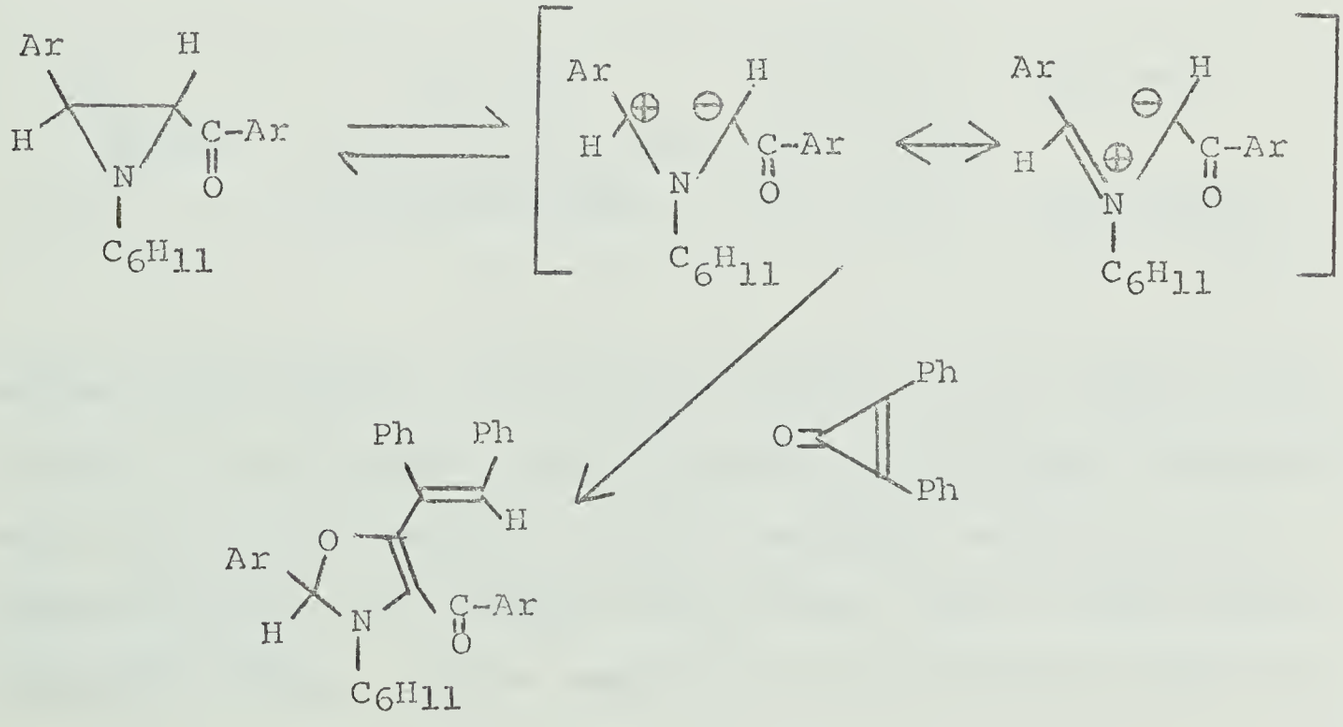
The reaction of tetrachlorocyclopentadiene with diphenylcyclopropenone also yields a derivative of the calicene system.[21]



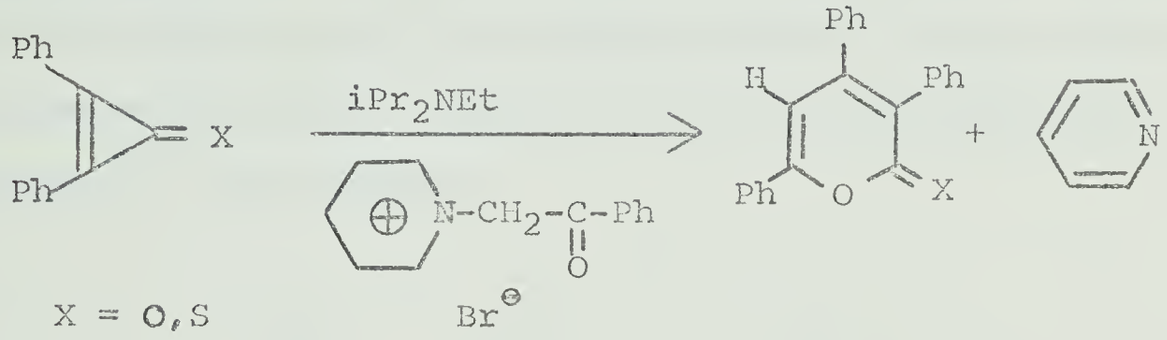
Izzo and Kende have also reported that diazomethane reacts as a 1,3-dipole in the presence of diphenylcyclopropenone, the product isolated being formed as a result of ring expansion.[22]



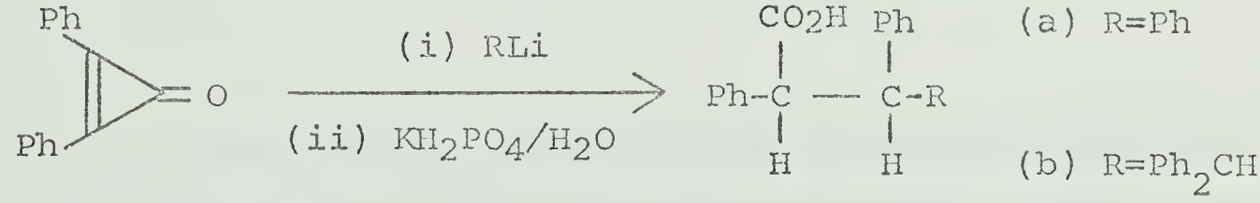
Recently, Lown and co-workers reported a novel synthesis of substituted 4-oxazolines by the addition of azomethine ylids derived from 2-aryl-3-aroylaziridines to diphenylcyclopropenone.[23] The 4-oxazolines are formed as a result of an initial 1,3-dipolar addition of the azomethine ylid at the carbonyl group of the cyclopropenone system.



Eicher and Hansen have shown that the reaction of pyridinium phenacylide, generated from N-phenacyl pyridinium bromide *in situ*, with diphenylcyclopropenone or diphenylcyclopropenethione results in the formation of a 2-pyrone derivative, by initial attack at the carbon-oxygen bond of the cyclopropene system.[24]



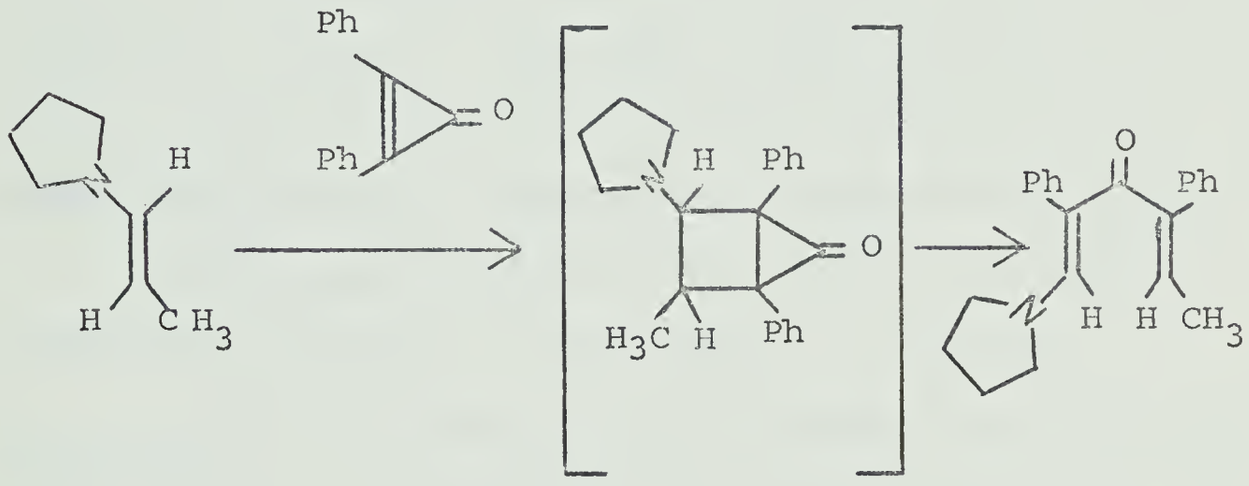
Recently, Ciabattoni, Kocienski and Melloni have carried out reactions which involve conjugate addition of organolithium reagents to diphenylcyclopropenone.[25] These reactions are summarised by the following scheme:-



Mechanistic pathways are discussed though it is clearly established by the authors that the production of these carboxylic acid derivatives requires initial conjugate addition of the organolithium to the carbon-carbon double bond of the cyclopropenone system. In the reaction of phenyllithium with di-

phenylcyclopropenone, 2,3-diphenylindenone (10%) is also produced. Deutero-labelling experiments have shown also that this product arises as a result of conjugate addition of phenyllithium to the carbon-carbon double bond.[25]

Berchtold and Ciabattoni have shown that diphenylcyclopropenone reacts with a variety of enamines to yield products which arise by an initial attack of the enamine at the carbon-carbon double bond of the cyclopropenone system.[26] For example:-



It was thought therefore that further knowledge was required in order to understand more fully the factors which control the mode of attack of nucleophiles on cyclopropenones. In addition, very little work has been reported concerned with 1,3-dipolar additions which involve cyclopropenones. The work described in subsequent chapters attempts to expand this knowledge.

II. RESULTS AND DISCUSSION

1. Reactions of Diphenylcyclopropenone with 1,3-Dipoles and Model Ylids.

Recently, Lown, Smalley and Dallas reported that the addition of azomethine ylids to diphenylcyclopropenone afforded 4-oxazolines, a novel heterocyclic system.[23]

The formation of 4-oxazolines by reaction of 2-aryl-3-aroyl substituted aziridines with diphenylcyclopropenone is postulated, as a result of an initial addition of the azomethine ylid across the carbon-oxygen bond of the cyclopropenone system.[23] This type of addition sharply contrasts that of diazomethane, where primary addition occurs at the carbon-carbon double bond of the cyclopropenone system.[22]

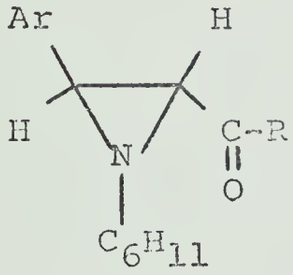
The work described in this section attempts to expand the knowledge of these types of reactions.

Six aziridines have been prepared and their reactions with diphenylcyclopropenone have been investigated. The aziridines, four of which have not been reported previously, were all prepared by well-established methods and their structures can be represented as shown by Table 1.

A. Aziridines

Aziridines (I) and (II). Biphenyl-4-aldehyde, prepared by a Gattermann reaction with biphenyl,[27] was condensed with the appropriate methyl ketone to give the corresponding α,β -unsaturated ketone. Bromination in chloroform solution, followed by treatment of the dibromo compound with

Table 1. General Description of Aziridines Used in this Research.



(cis/trans mixtures)

(I) Ar = p-biphenylyl, R = Ph

(II) Ar = p-biphenylyl, R = Me

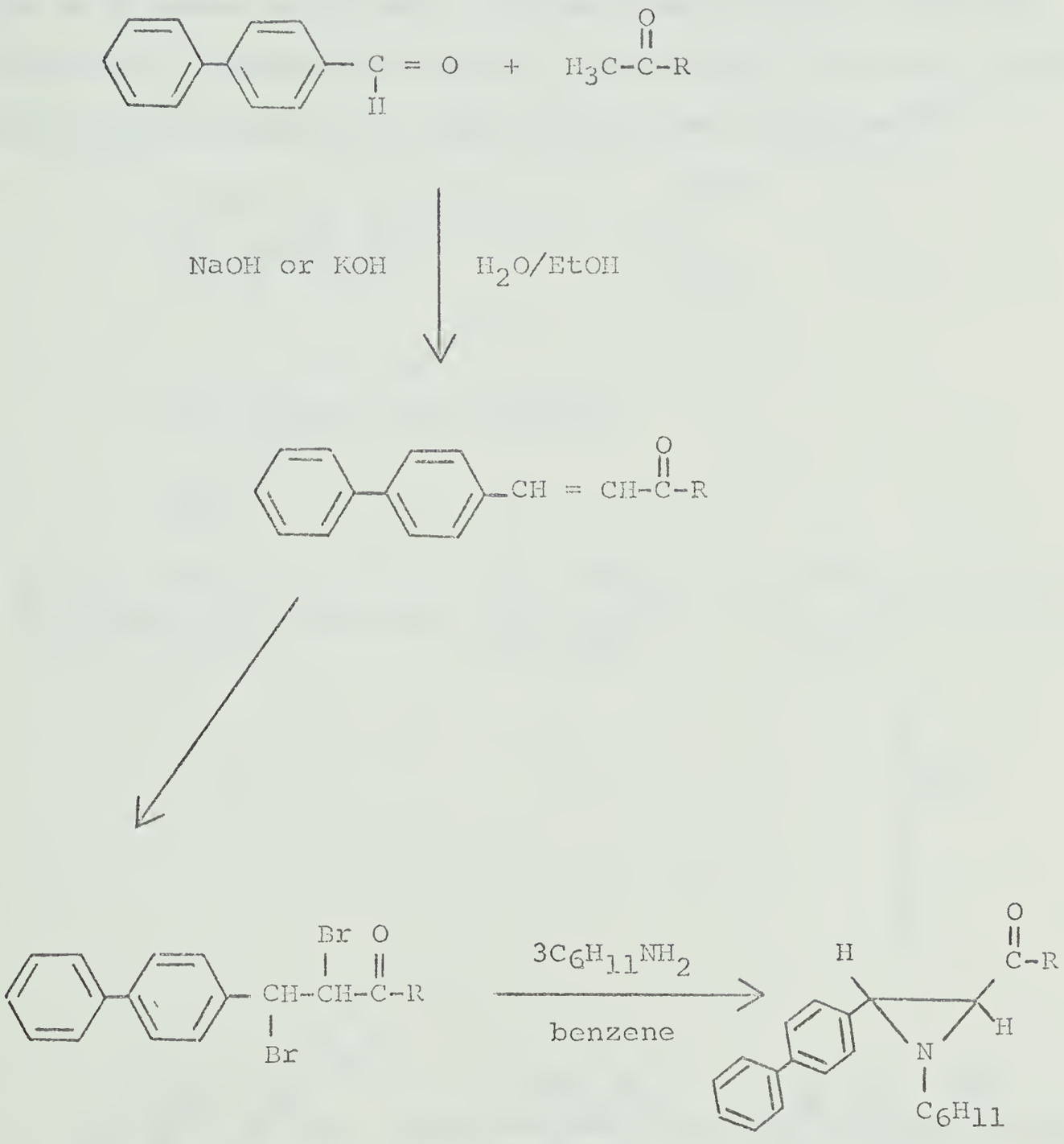
(III) Ar = p-biphenylyl, R = OMe

(IV) Ar = Ph , R = OMe

(V) Ar = Ph , R = OEt

(VI) Ar = Ph , R = OiPr

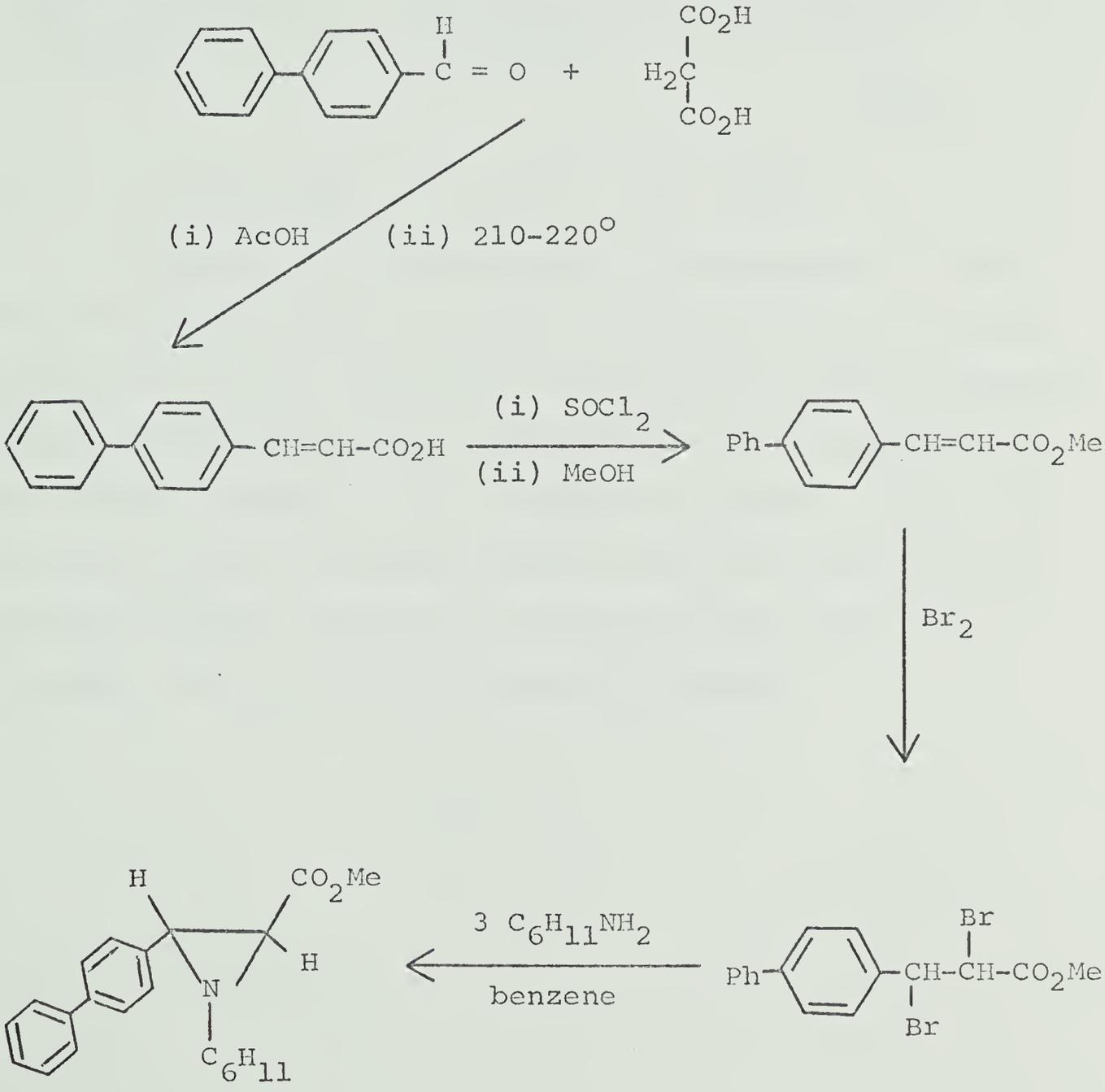
cyclohexylamine in benzene, gave the desired aziridine in good yield.



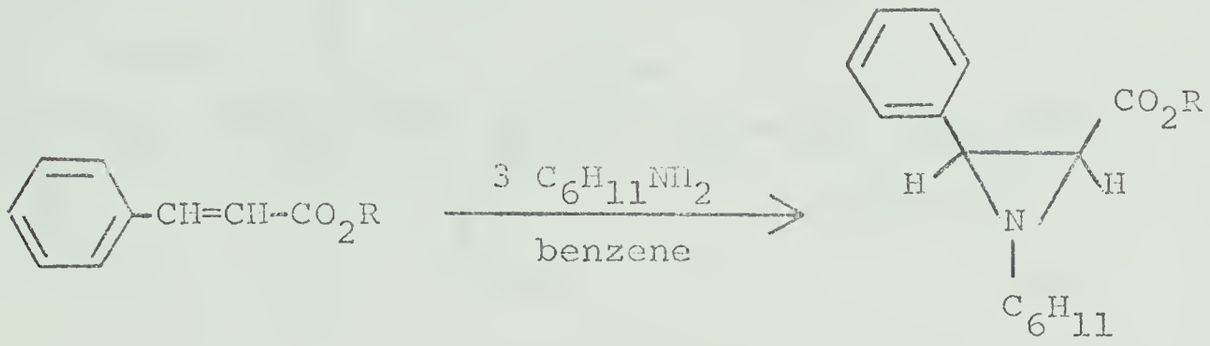
(I) R = Ph

(II) R = Me

Aziridine (III) was prepared in similar manner to aziridines (I) and (II). Biphenyl-4-aldehyde was condensed with malonic acid, and the product was decarboxylated to yield the α,β-unsaturated acid. After esterification, and bromination in chloroform solution, the dibromo ester was treated with cyclohexylamine to yield the desired aziridine.[28]

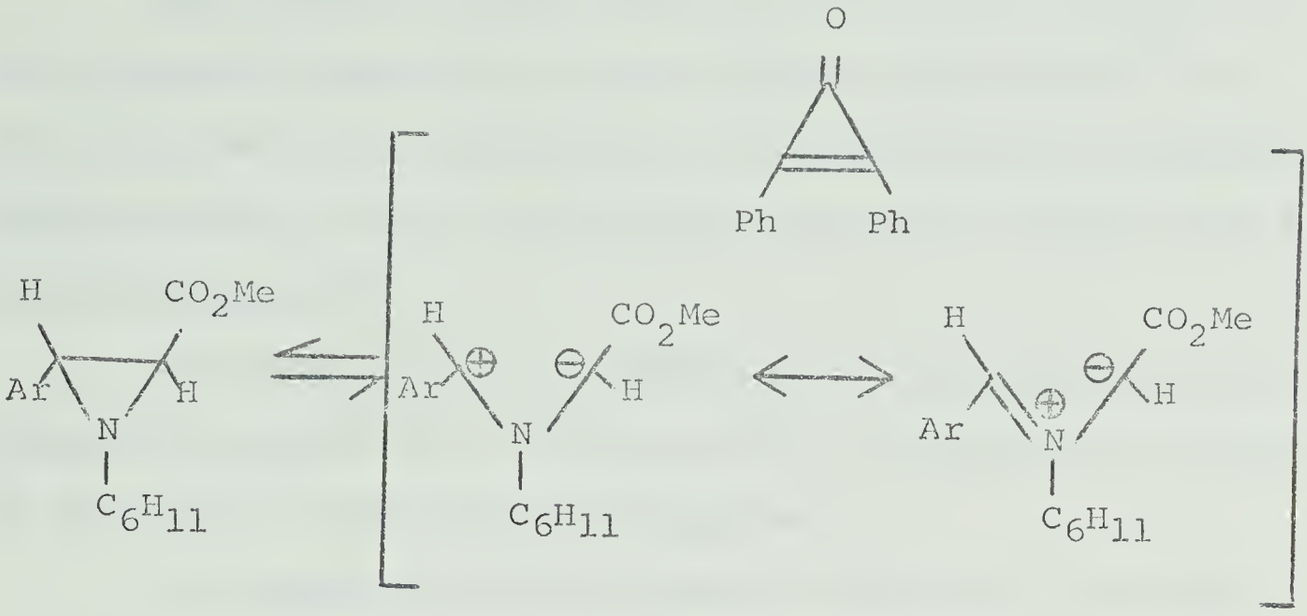


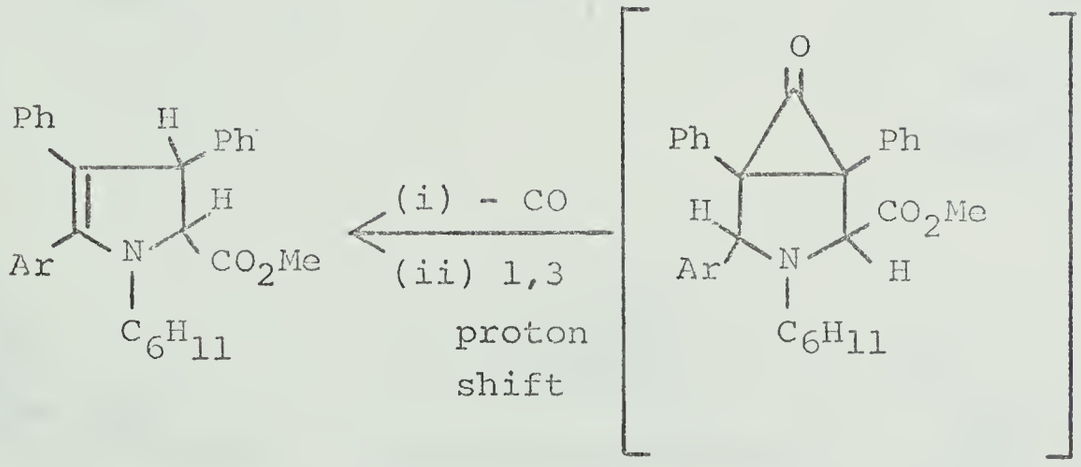
Aziridines (IV), (V) and (VI) were all prepared from the appropriate cinnamic acid esters as described by the following scheme:-



R = Me (IV) Et (V) , iPr (VI).

Reaction of 2-p-biphenylyl-3-carbomethoxy-1-cyclohexylaziridine (III) with diphenylcyclopropenone in benzene solution at reflux, afforded a good yield of the 2,3-dihydropyrrole derivative (VII). The reaction can be envisaged as proceeding initially via a 1,3-dipolar addition of the azomethine ylid to the carbon-carbon double bond of the cyclopropenone system followed by decarbonylation and proton transfer, according to the following scheme:-



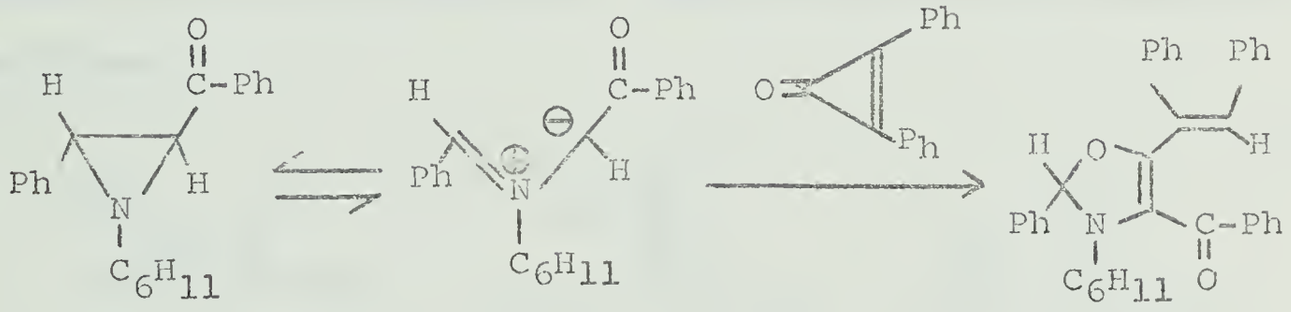


(VII) Ar = p-biphenylyl

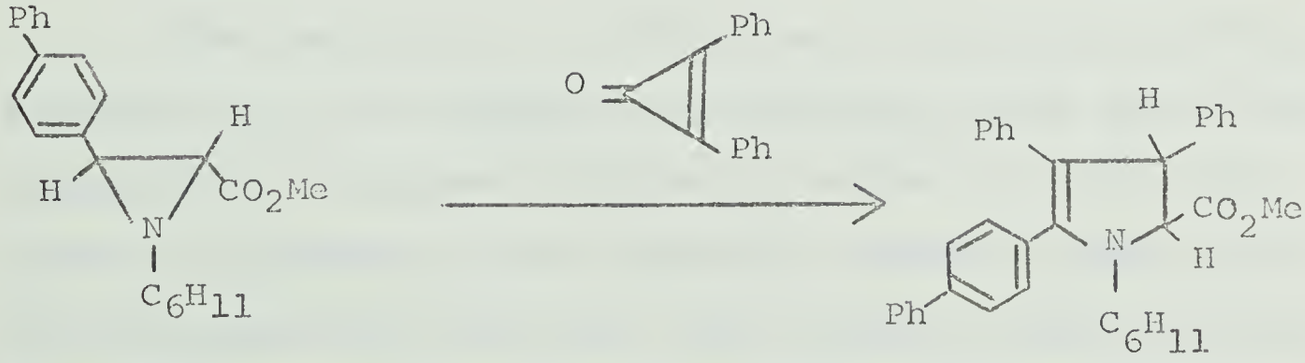
The course of this reaction is in sharp contrast to that reaction reported by Lown, Smalley and Dallas.[23] It also contrasts with the addition of diazomethane to diphenylcyclopropenone, where a ring expansion occurs rather than a decarbonylation.[22]

It became necessary therefore, to investigate which structural properties of the aziridine controlled the course of addition to diphenylcyclopropenone.

A comparison of the course of addition of the two azomethine ylid types can be summarised as follows:-

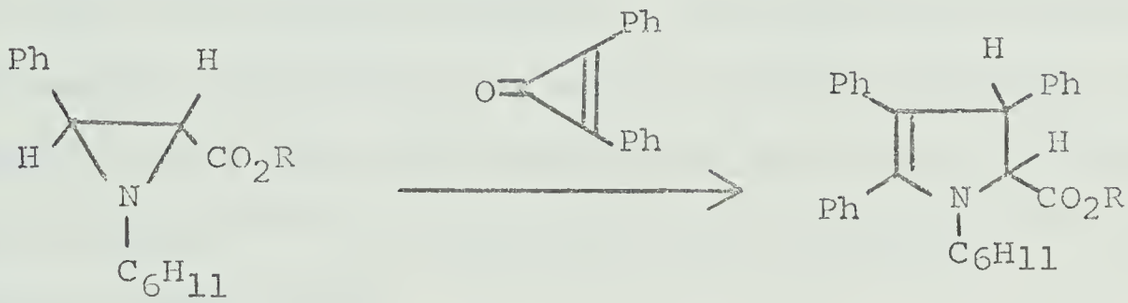


substituted
4-oxazoline (XV)



The differences in structure of the azomethine ylids lie in the nature of both the 2- and 3-substituents of the aziridine. For this reason, 3-carbomethoxy-1-cyclohexyl-2-phenylaziridine (IV) was prepared in which the nature of the 2-substituent, is identical to that in the aziridine, which afforded a 4-oxazoline, in its reaction with diphenylcyclopropenone.

It was found that the reactions of the 3-carboalkoxy-1-cyclohexyl-2-phenylaziridines (IV), (V) and (VI), with diphenylcyclopropenone, all result in the formation of derivatives of 2,3-dihydropyrrole. These reactions are summarised as shown:-



R = Me (VIII); Et (IX), iPr (X)

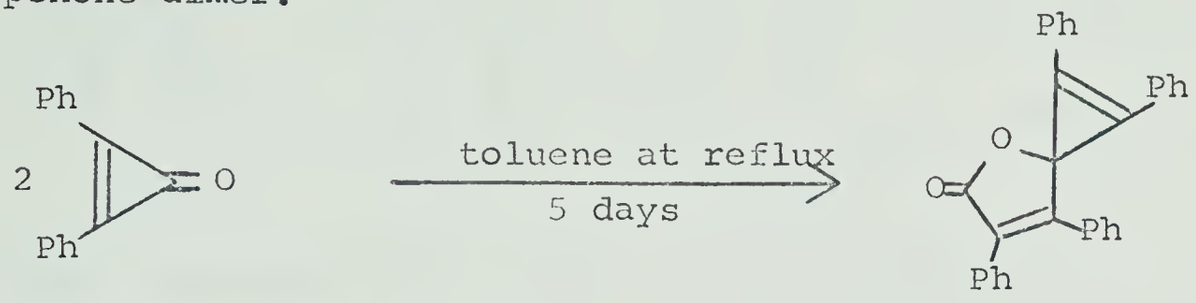
The reaction of 3-carbomethoxy-1-cyclohexyl-2-phenylaziridine (IV) with diphenylcyclopropenone could not be achieved successfully in benzene solution at reflux. In this case, diphenylcyclopropenone was recovered unchanged (68%) and the 2,3-dihydropyrrole derivative was obtained in only 9.9% yield. A higher yield of (VIII) (85.8%) was given by reaction in toluene solution at reflux.

It was concluded from these observations that the 2-p-biphenylyl substituted aziridine undergoes 2,3-scission more readily than the aziridine having the 2-phenyl substituent, due to a greater delocalisation of the positive charge.

The course of these reactions which produce derivatives of 2,3-dihydropyrrole was checked by reactions of aziridines (III) and (IV) with diphenylacetylene in toluene solution at reflux. In both cases, identical products to those given by reaction with diphenylcyclopropenone were produced (VII) and (VIII), though in lower yields. The reason for the lower yields is readily explained in that diphenylcyclopropenone is a much more reactive dipolarophile than is diphenylacetylene. The reactions of aziridines with reactive dipolarophiles such as dimethylacetylene dicarboxylate has been well established by the work of Heine and co-workers,[29,30] by Padwa and his co-workers,[31,32] and also by Huisgen.[33,34]

Conceivably decarbonylation of diphenylcyclopropenone to diphenylacetylene could occur prior to reaction with the azomethine ylids described. However this can be ruled out because Breslow and co-workers have shown that decarbonylation of diphenylcyclopropenone occurs only at temperatures in the range of 160°.[7] Also Lown has shown that prolonged heating of diphenylcyclopropenone in toluene solution at

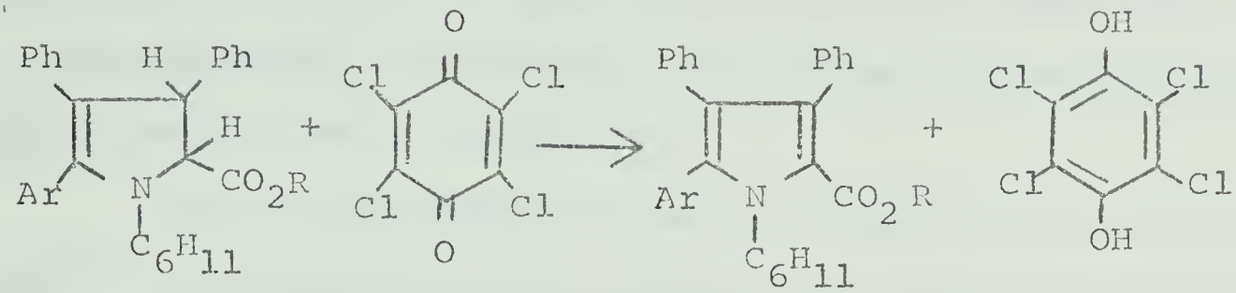
reflux, results in the formation of a diphenylcyclopropenone dimer.[15]



The proposed structures of the 2,3-dihydropyrrole derivatives (VII), (VIII), (IX) and (X) were based on their proton magnetic resonance, infrared absorption and mass spectra and elemental analysis.

In their proton magnetic resonance spectra, these compounds all show an AB quartet centred at approximately δ 5.4 and δ 5.7, due to the 2 and 3 protons. A coupling constant of 6Hz., and 7Hz. in the case of (IX), indicated a cis arrangement for the protons about the 2,3 carbon-carbon bond.[30] Further it was observed that under conditions of electron impact in the mass spectrum these compounds dehydrogenated and showed base peaks which corresponded to the pyrroles.

Further verification of these structures was obtained by chemical dehydrogenation using p-chloranil in dry chlorobenzene at reflux, a method well established by Heine and co-workers.[30] The compounds (VII) and (X) were subjected to this treatment according to the following scheme:-



(VII) Ar=p-biphenylyl; R=Me. (XI) Ar=p-biphenylyl; R=Me.

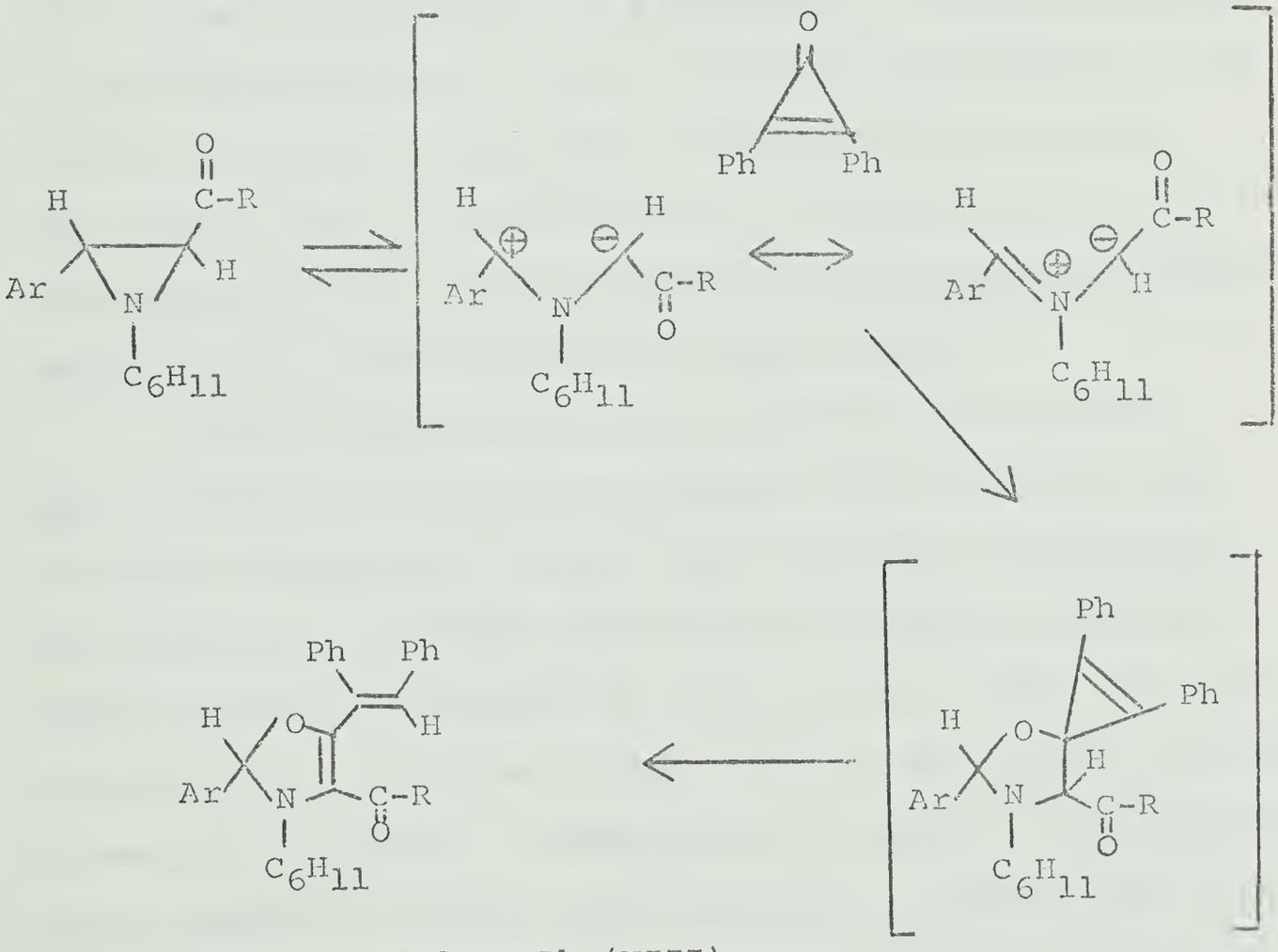
(X) Ar=Ph; R=iPr. (XII) Ar=Ph; R=iPr.

Examination of the infrared spectrum of, for example, compound (VII), showed a carbonyl stretching frequency of 1725 cm^{-1} (C=O of an ester) whereas the comparable stretching frequency in the dehydrogenated material (XI) was at 1698 cm^{-1} (α,β -unsaturated C=O of an ester). The postulated positions of the hydrogen atoms in (VII) were thus substantiated by this marked change in the values of the carbonyl stretching frequencies. Further, fragmentation of compound (VII) in the mass spectrum showed a strong peak at m/e 454 which corresponds to $[M-(COOCH_3)]$. This fragmentation can only be explained by the proposed structure with a proton α- to the carbomethoxy group. No peak was shown in the mass spectrum corresponding to a loss of the biphenylyl group from the molecular ion.

Next it became necessary to examine the influence of the 3-substituent of the aziridine, upon the course of addition of azomethine ylids to diphenylcyclopropenone. For this reason aziridines (I) and (II) were prepared where the

2-p-biphenylyl substituent was maintained but where the group in the 3-position was changed from carboalkoxy to benzoyl and acetyl substituents respectively.

In both reactions studied with diphenylcyclopropenone, products resulted which corresponded to that type of addition reported by Lown, Smalley and Dallas, namely the production of substituted 4-oxazolines. The reactions were carried out in benzene solution at reflux and the reactions rationalised as outlined below:-



Ar = p-biphenylyl, R=Ph (XIII)

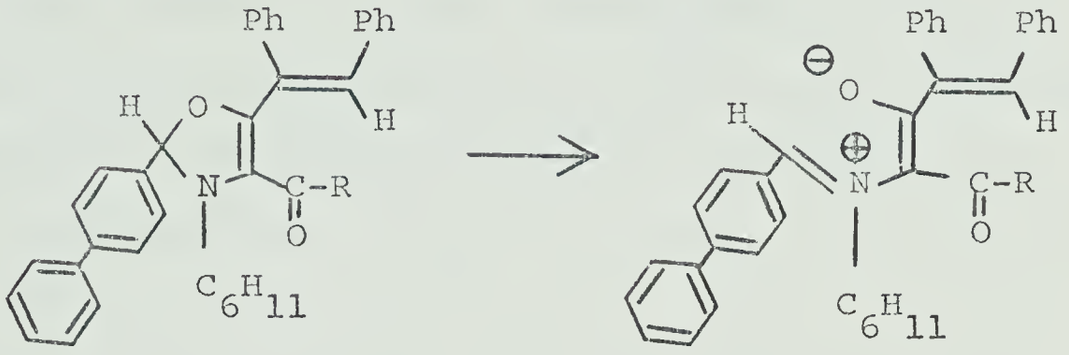
Ar = p-biphenylyl, R=Me (XIV)

It is worthy to note at this point that in the case where R=Ph, the yield of 4-oxazoline (XIII) derivative was quantitative.

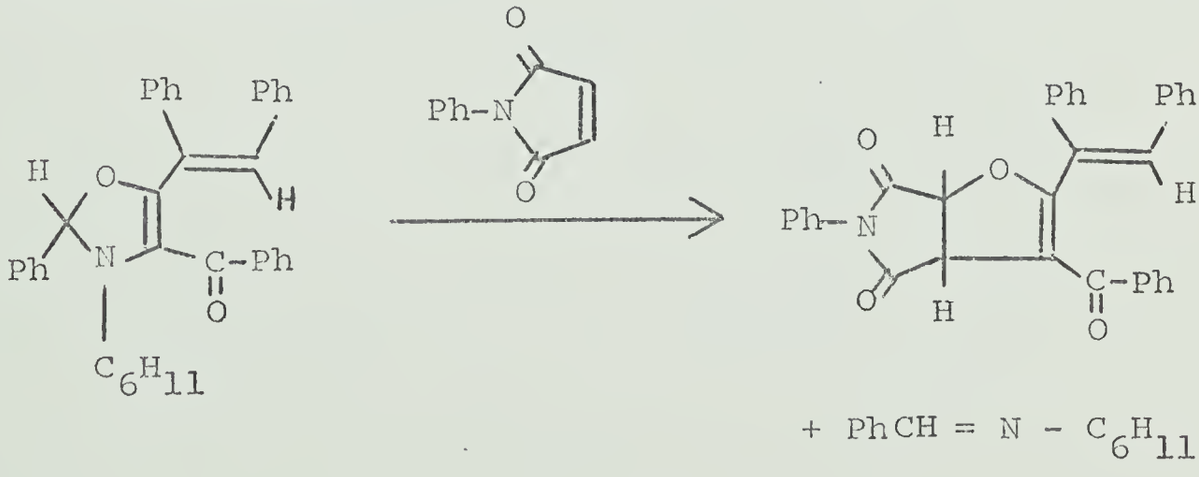
These 4-oxazolines (XIII) and (XIV) were characterised by their proton magnetic resonance, infrared and mass spectra and elemental analysis. In their proton magnetic resonance spectra both (XIII) and (XIV) show a singlet at approximately δ5.0 which is assigned to the benzylic proton in the 2-position of the 4-oxazoline. The assignment of a cis stereochemistry of the 1,2-diphenylvinyl group in the 5-position of the 4-oxazoline, is supported by the fact that Breslow and his co-workers have demonstrated that the nucleophilic ring-opening of diphenylcyclopropenone results exclusively in the formation of a cis product.[7]

These 4-oxazolines both exhibited thermochromic and photochromic properties although (XIII) which has the 4-benzoyl substituent is much more intensely thermochromic upon melting than (XIV) which has the 4-acetyl substituent. Allied to this observation is the fact that (XIII) was never obtained as a colourless solid, and even when freshly prepared it was pink in colour. Compound (XIV) could be crystallised from ethanol as a white solid although it slowly turned pink on exposure to light and also it gave a red melt though not as intensely coloured as the melt given by (XIII).

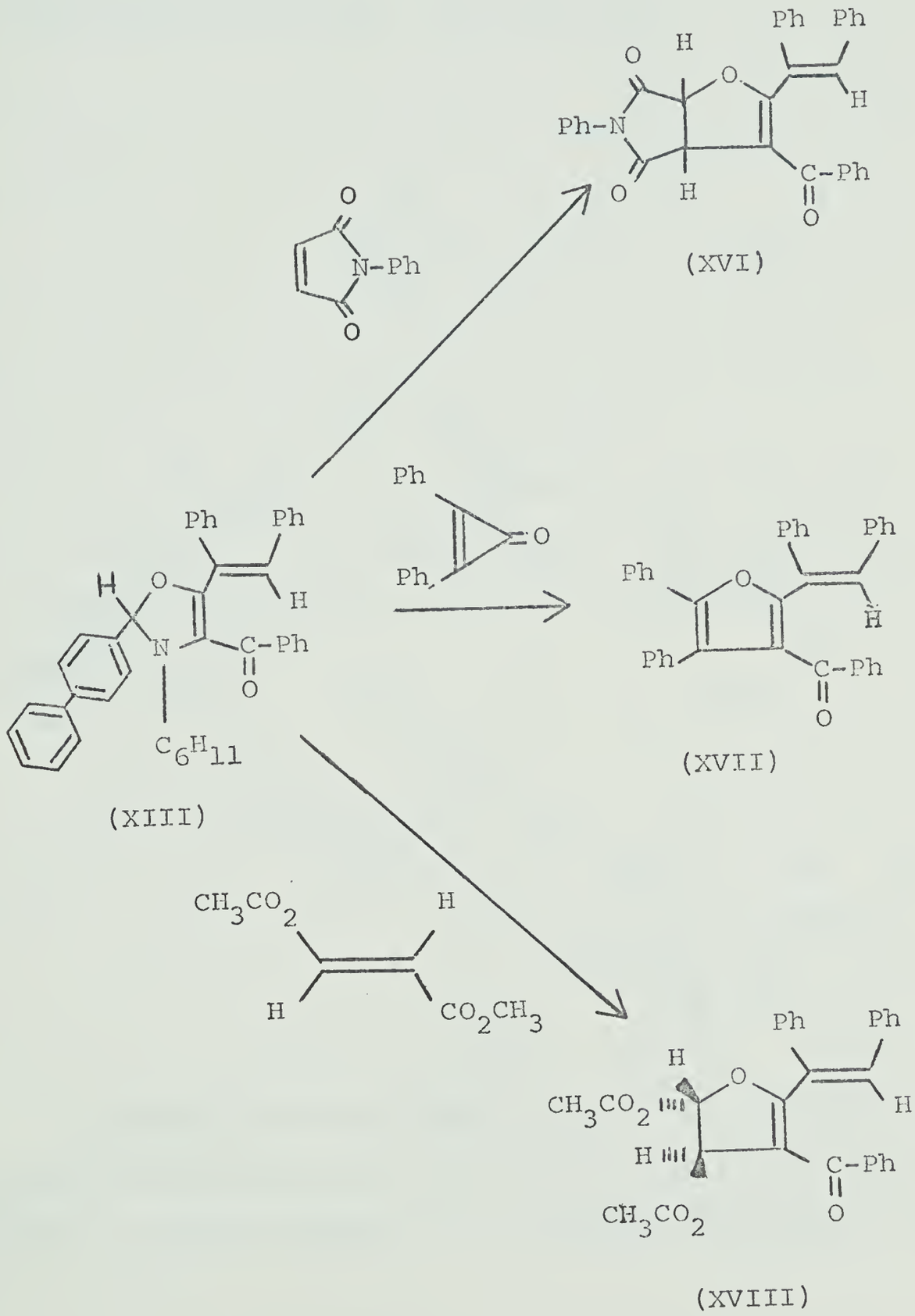
The photochromism, and thermochromism observed upon melting of these oxazolines, are tentatively attributed to the open-chain form as shown below:-



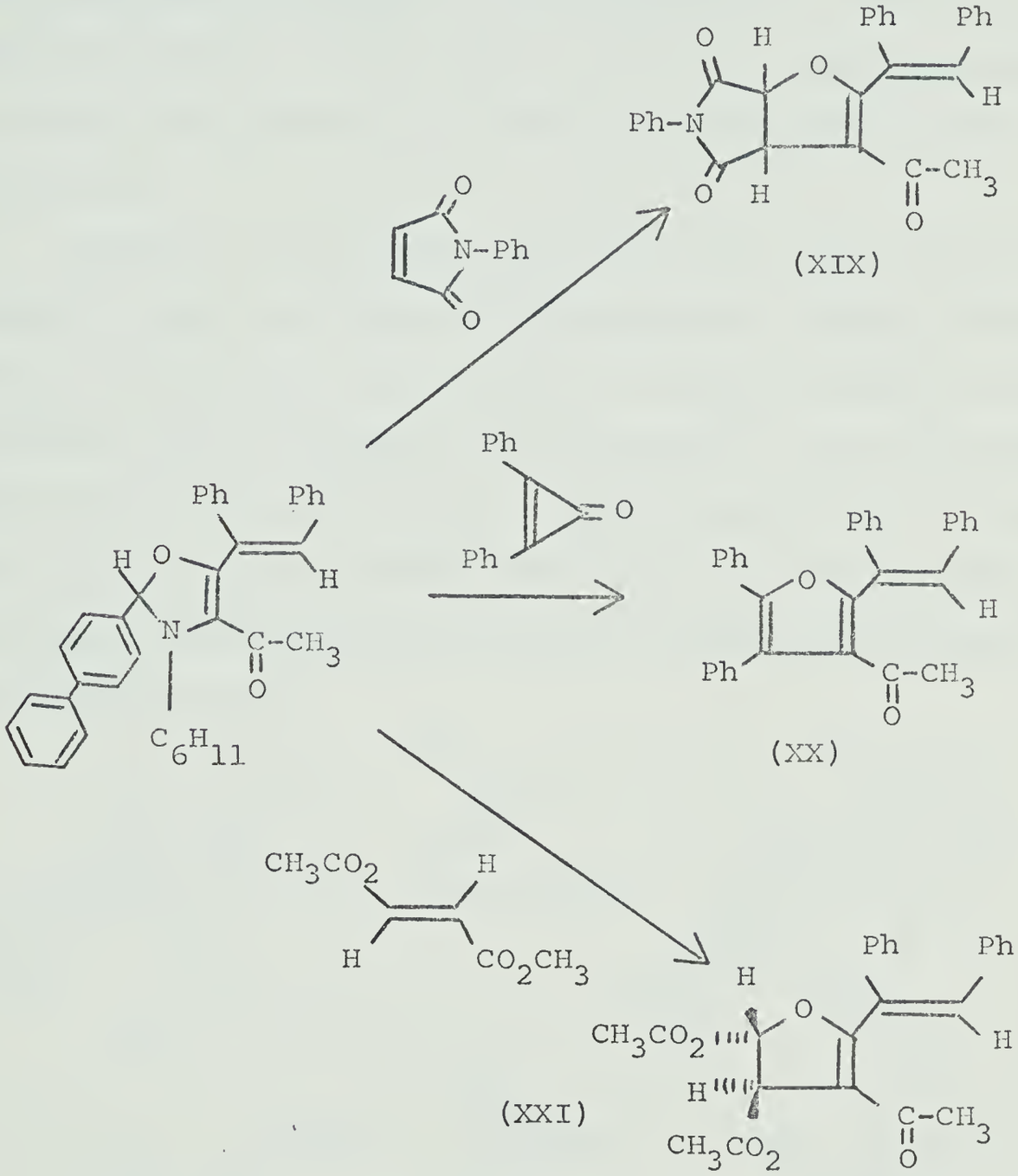
It was anticipated that the new azomethine ylids derived from 4-oxazolines would react with suitable dipolarophiles by a [2 + 3] cycloaddition to yield derivatives of furan. Lown, Smalley and Dallas have shown that 4-benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline (XV) reacts with N-phenylmaleimide, for example, according to the following scheme:-[23]



It was anticipated that the 4-oxazoline (XIII) should give identical furan derivatives to those given by (XV) above, as the structures of these 4-oxazolines differ only in the nature of the substituent in the 2-position. Thus in the reaction of these 4-oxazolines (XIII) and (XV) with dipolarophiles, only the nature of the extruded anil moiety is different, while the structures of the $[2 + 3]$ cycloadducts should be the same. This was found to be the case, and furan derivatives (XVI), (XVII) and (XVIII) have been prepared from the 4-oxazoline (XIII) which were found to be identical in all respects to those compounds previously reported by Lown, Smalley and Dallas who have prepared the same furan derivatives by using the 4-oxazoline (XV).[23, 35, 36] This work further supports the proposed structures of the 4-oxazolines, and can be summarised by the following chart:-


Ph Ph
H
O
O
Ph-N
O
H
C-Ph
O
H
(XVI)
O
N-Ph
O
Ph
Ph
O
Ph
Ph Ph
Ph
O
H
N
C-Ph
O
H
Ph
C-Ph
O
C_6H_{11}
(XVII)
(XIII)
CH_3CO_2
H
H
CO_2CH_3
Ph Ph
H
O
CH_3CO_2
H
H
C-Ph
O
CH_3CO_2
(XVIII)

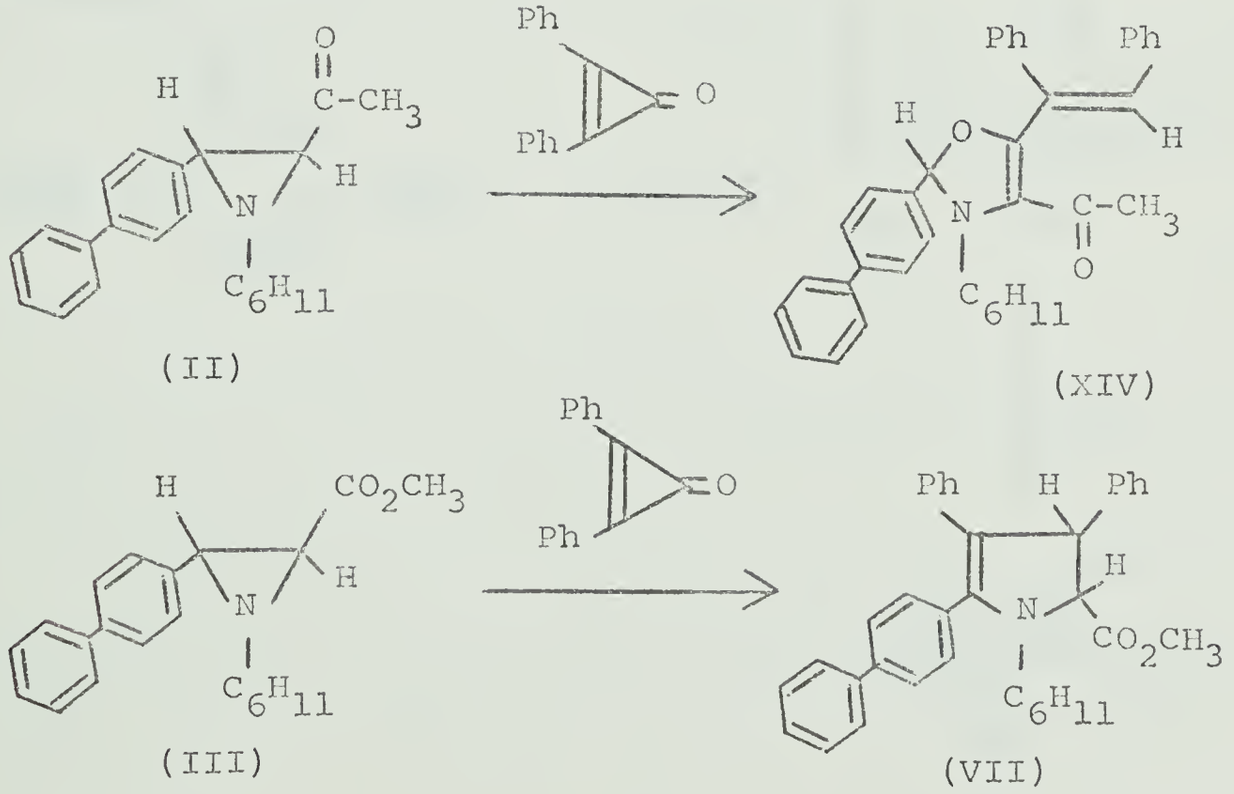
Similarly the 4-acetyl substituted 4-oxazoline (XIV) was treated with the same dipolarophiles to give a series of new furan derivatives (XIX), (XX) and (XXI).



Reactions of the 4-oxazolines (XIII) and (XIV) to give the tetrasubstituted furans (XVII) and (XX) respectively, represent further examples of 1,3-dipolar additions to the

carbon-carbon double bond of diphenylcyclopropenone. It was also noted that the addition of these 4-oxazolines (XIII) (XIV) to dimethyl fumarate gave stereospecific addition in which the geometry of the groups exhibited a trans arrangement about the 2- and 3-positions of the 2,3-dihydrofuran derivatives.

Thus it was realised from this work, that the substituent in the 3-position of the aziridine, namely carboalkoxy or aroyl/acyl, determined the course of addition of azomethine ylids to diphenylcyclopropenone. The most striking difference can be seen using as examples aziridines (II) and (III), and as has been shown previously, the former gives rise to a substituted 4-oxazoline and the latter a substituted 2,3-dihydropyrrole.

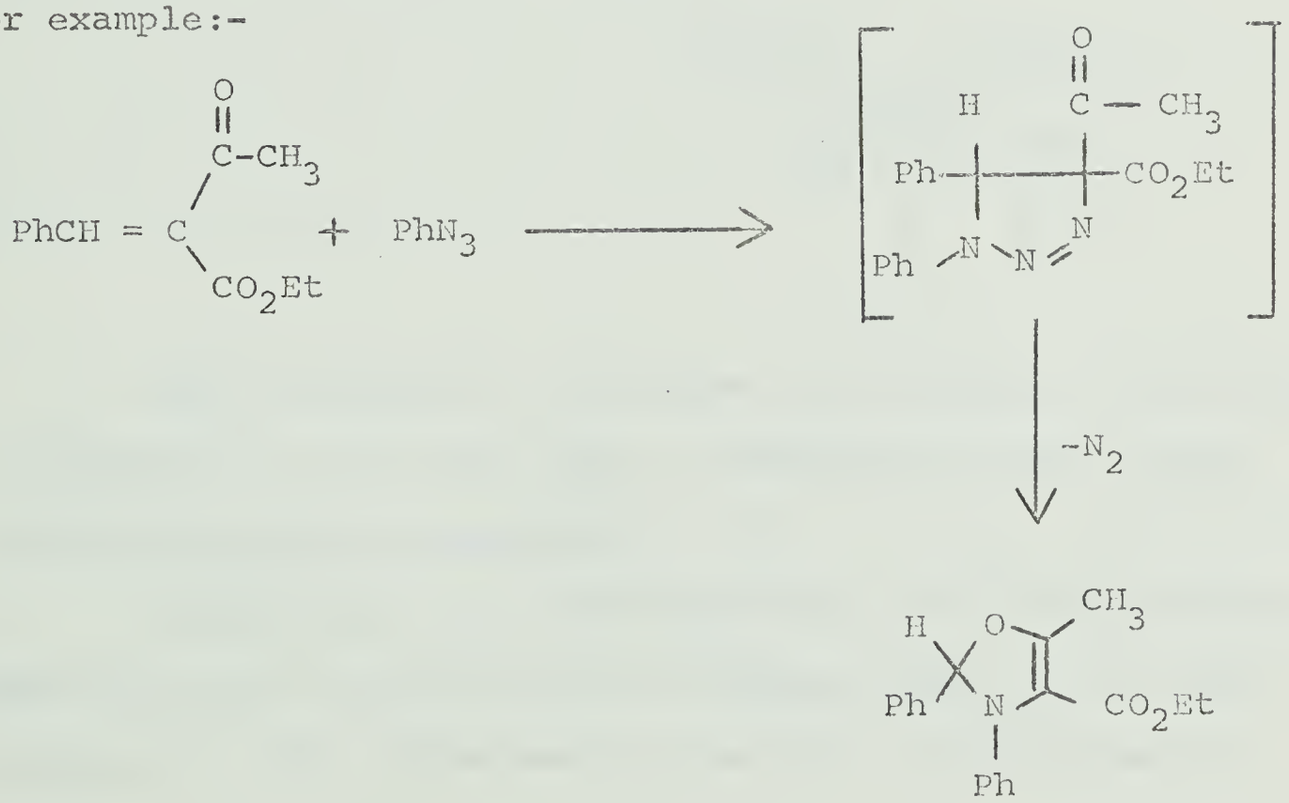


(II) (XIV)

(III) (VII)

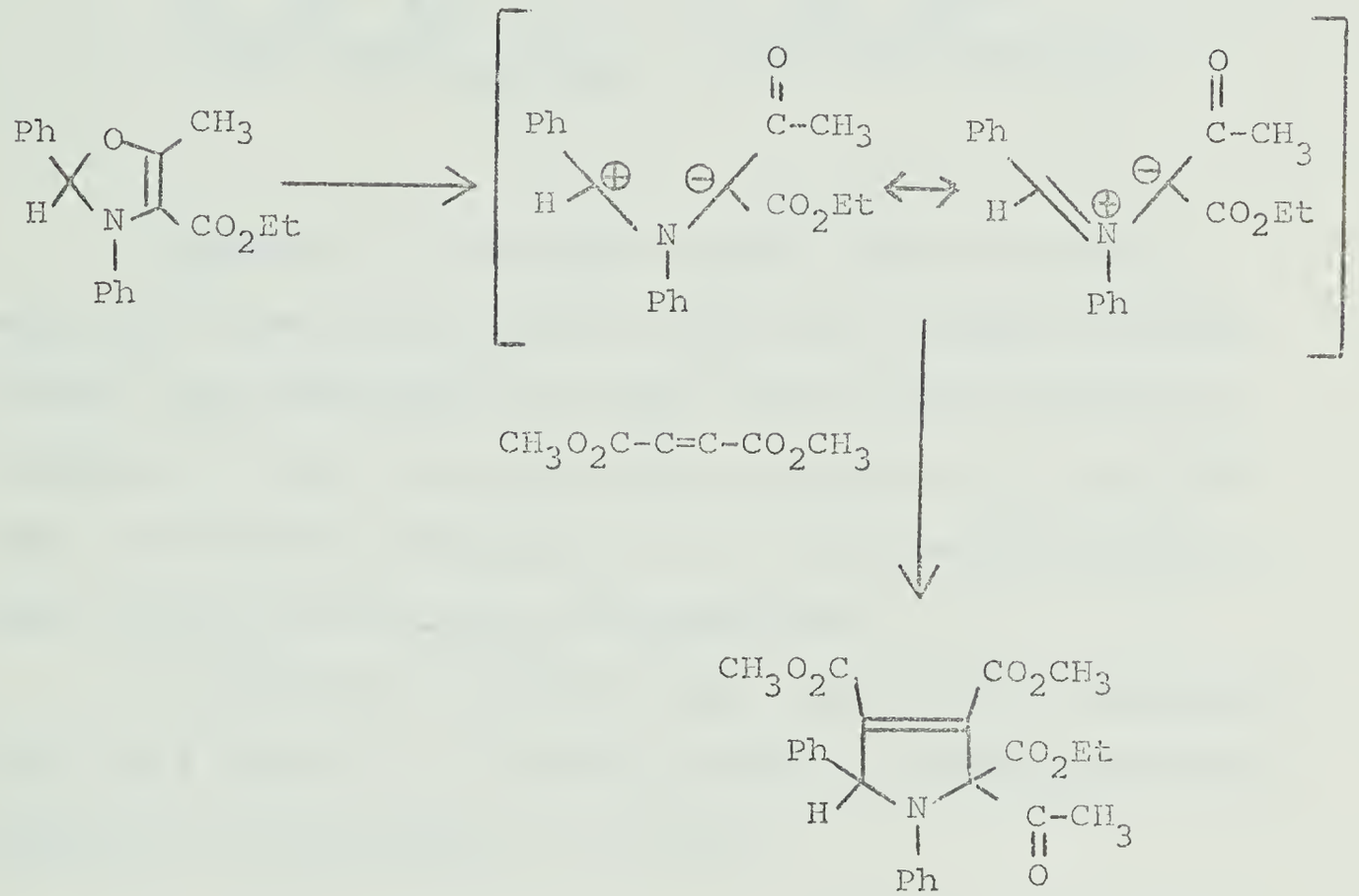
No instances of mixtures of these products were observed in the examples cited. It is difficult to envisage any fundamental difference in the properties of the two azomethine ylid types, though this possibility cannot be ruled out. At this point it can only be tentatively suggested that the course of addition of azomethine ylids, of the types described, to diphenylcyclopropenone is dependent upon steric factors or more likely upon the relative stabilities of the products. In support of this, related results have been obtained by Texier and Carrie.[37] They found that α,β-unsaturated ketones react with arylazides in certain instances, to give very unstable 4-oxazolines which had previously been assigned the 4-isoxazoline structure incorrectly.[38]

For example:-



(A)

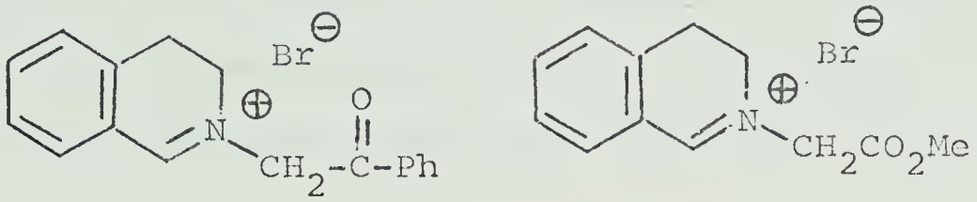
The 4-oxazolines are isolable only at low temperatures and under nitrogen. Compound (A) reacts with acetylenic esters to give pyrrole derivatives rather than derivatives of furan.[37]



It is difficult to envisage any intrinsic differences in properties of the two types of azomethine ylids derived from the aziridines described.

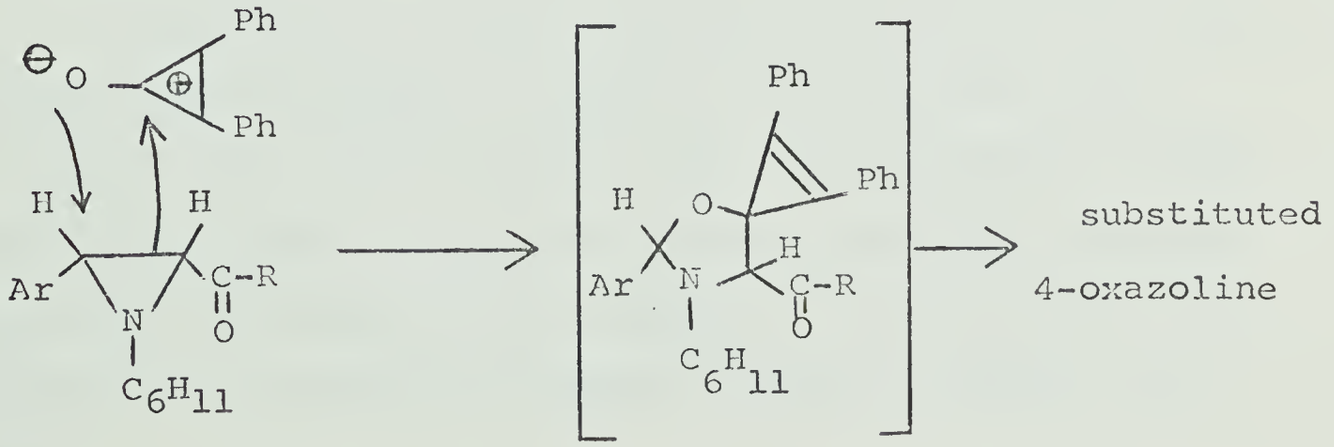
Experiments have been carried out which were thought might give some indication as to whether there is, in fact, a reason for this difference in reaction. Quaternisation

of 2,3-dihydroisoquinoline with (a) phenacyl bromide and (b) methyl bromoacetate afforded the two quaternary salts as shown below:-[39]

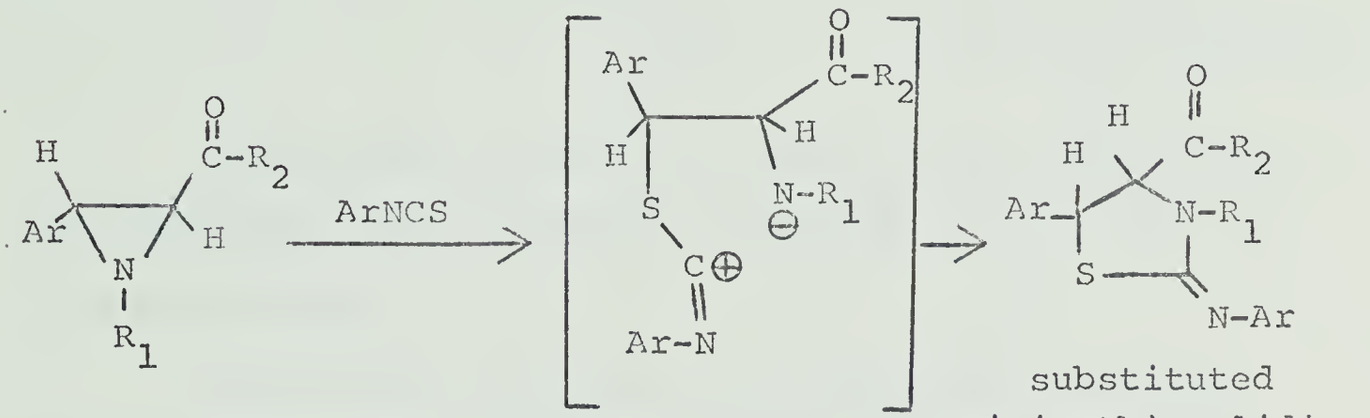


Treatment of these salts with a tertiary amine would give rise to azomethine ylids which closely resemble the two types described which are derived from aziridines. Reactions of this nature have been carried out in the presence of diphenylcyclopropenone, but the gum-like products have not been successfully characterised.

It could be considered that substituted 4-oxazolines arise as a result of an initial attack by diphenylcyclopropenone as an O-nucleophile as shown:-

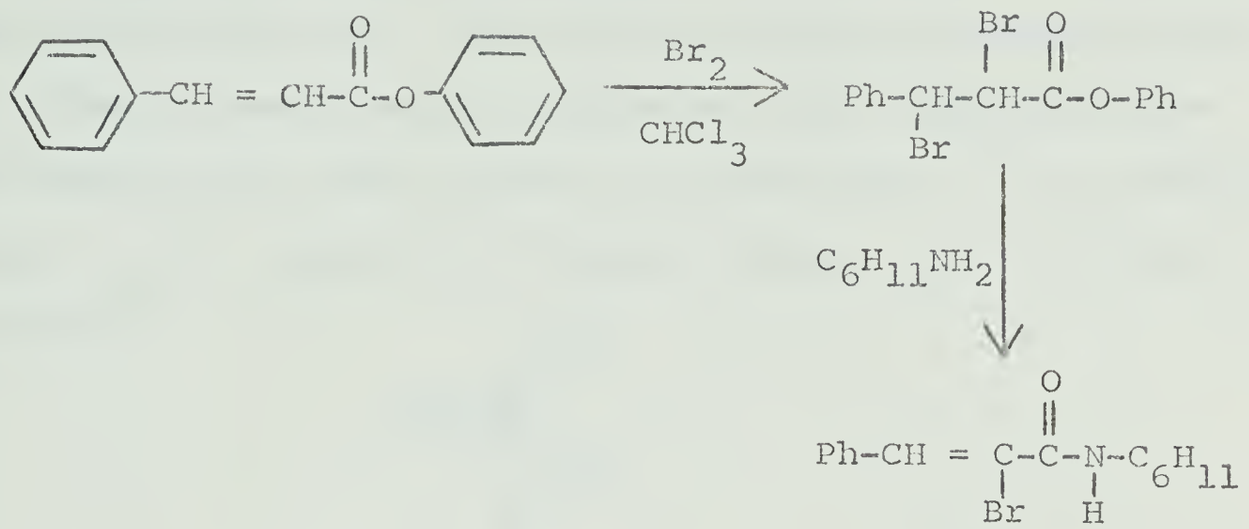


This possibility can be discounted on the basis of the work of Lown and co-workers who have shown that the reactions of strong nucleophiles such as aryl isothiocyanates with aziridines result in the formation of iminothiazolidines.[40] This type of product arises by cleavage of the 1,2 bond of the aziridine ring rather than the 2,3 bond as shown:-



A number of attempts were made to prepare 3-carbophenoxy-1-cyclohexyl-2-phenylaziridine in order to further expand the knowledge of additions of azomethine ylids to diphenylcyclopropenone.

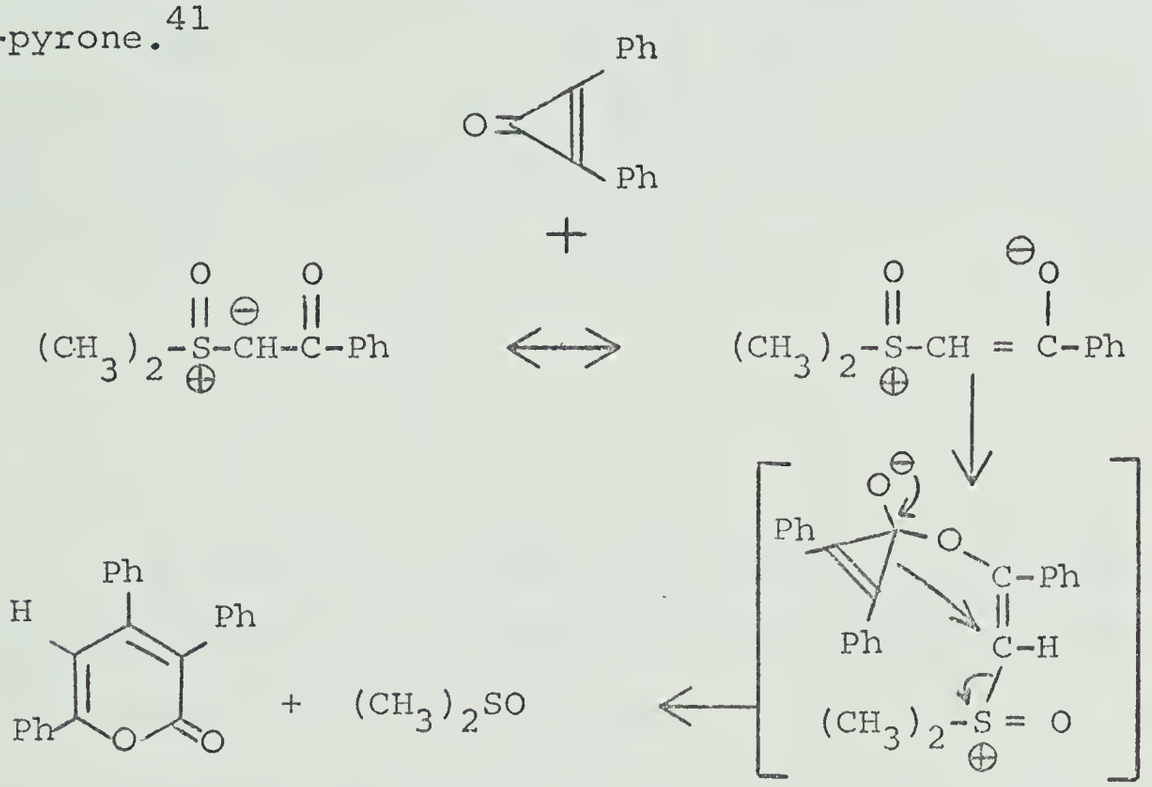
Bromination of phenyl cinnamate in chloroform solution proceeded smoothly to yield the α,β-dibromo ester. Reaction of this dibromo ester with cyclohexylamine in benzene solution did not yield the desired aziridine, however, the product isolated in all instances, was identified unambiguously as 2-bromo-N-cyclohexyl-3-phenyl propenoic acid amide.



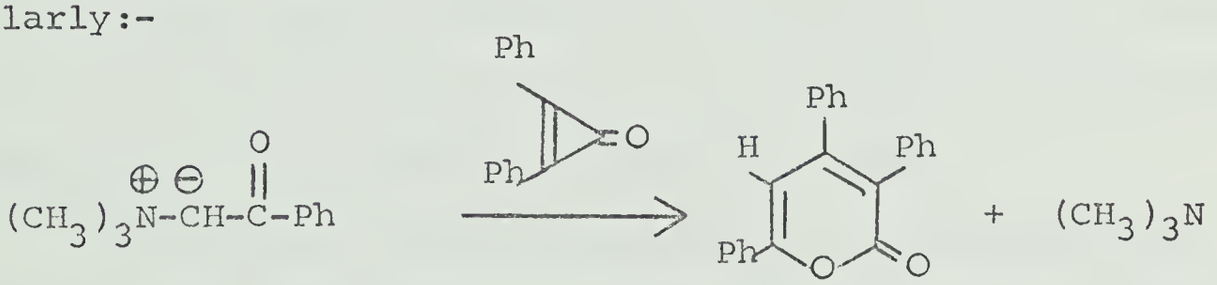
This product arose as a result of the lability of the phenoxide anion under the influence of bases such as cyclohexylamine.

Relatively little was known about the behaviour of cyclopropenones with nucleophiles. However, it has been established that attack occurs either at the carbon-oxygen bond or the carbon-carbon double bond of the cyclopropenone system, which parallels our findings with 1,3-dipoles. Eicher has shown that the reaction of N-phenacylpyridinium bromide with diphenylcyclopropenone in the presence of diisopropylethylamine results in a good yield of 3,4,6-triphenyl-2-pyrone.[24] This product was explained as a result of a nucleophilic attack of the ylid at the carbon-oxygen bond of the cyclopropenone system.

Lown has extended this type of reaction by using other stabilized ylids. Reactions of diphenylcyclopropenone with trimethylammonium phenacylide and with dimethylsulfoxonium phenacylide both resulted in good yields of an identical product to that reported by Eicher, namely, 2,4,6-triphenyl-2-pyrone.[41]

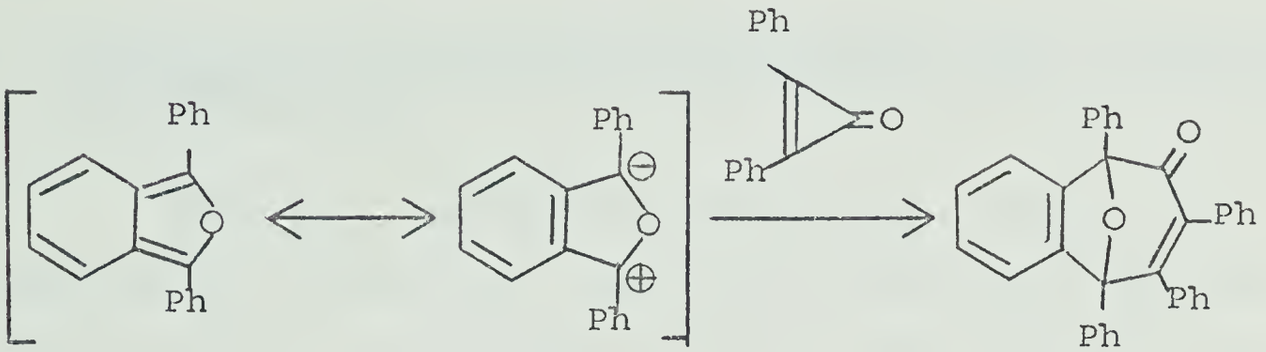


Similarly:-



Lown has also shown that reaction of diphenylisobenzofuran with diphenylcyclopropenone results in the formation of a product explained by attack of the potential 1,3-dipole at the carbon-oxygen bond of the cyclopropenone

system. This reaction is outlined below.[41]



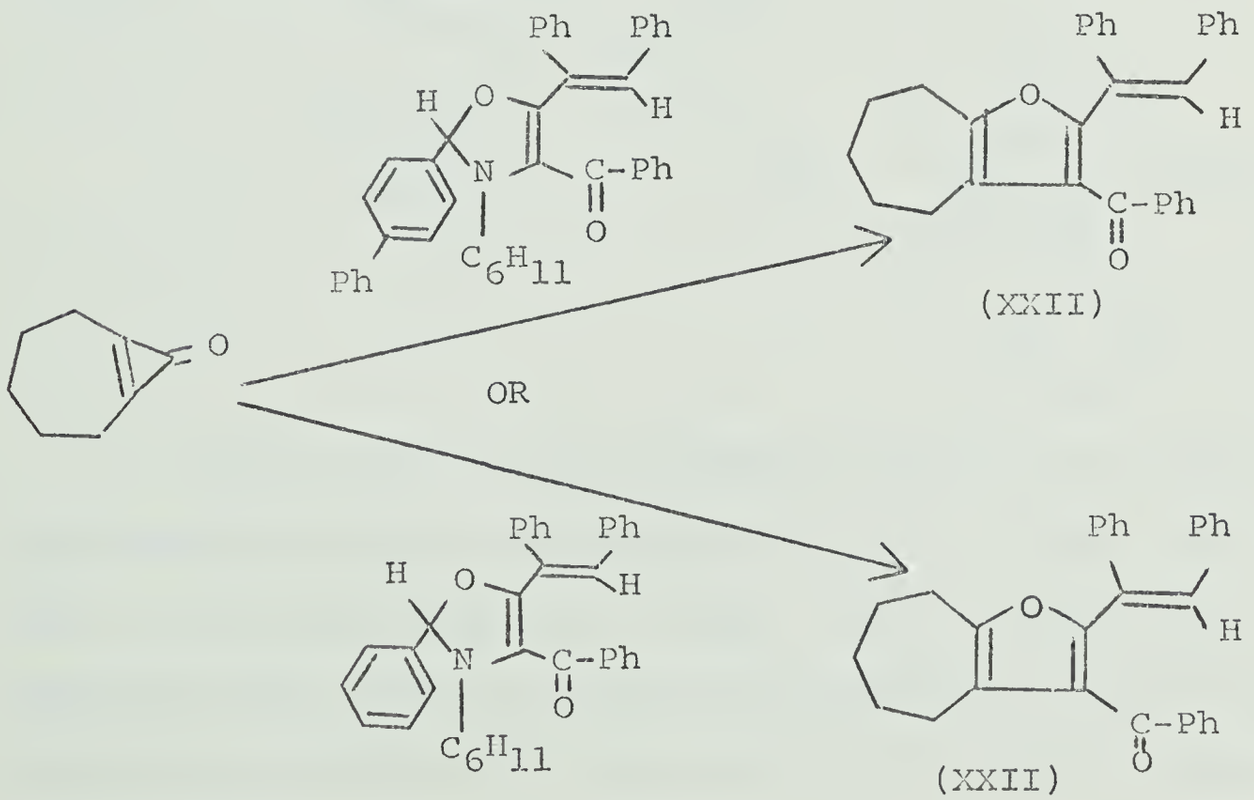
A number of attempts were made to effect reaction of N-pyridiniumdibenzoyl methide with diphenylcyclopropenone under varying conditions. In all instances, the starting materials were recovered unchanged. The reasons for this result can be tentatively explained by steric factors or more probably in terms of the weak nucleophilic character of this particular internally stabilised ylid.

The results obtained by reactions of diphenylcyclopropenone with 1,3-dipoles and with model ylids have indicated that the carbon-oxygen bond and the carbon-carbon double bond of the cyclopropenone system have a comparable reactivity. It became necessary therefore to see if varying the nature of the substituents on the cyclopropenone system had any

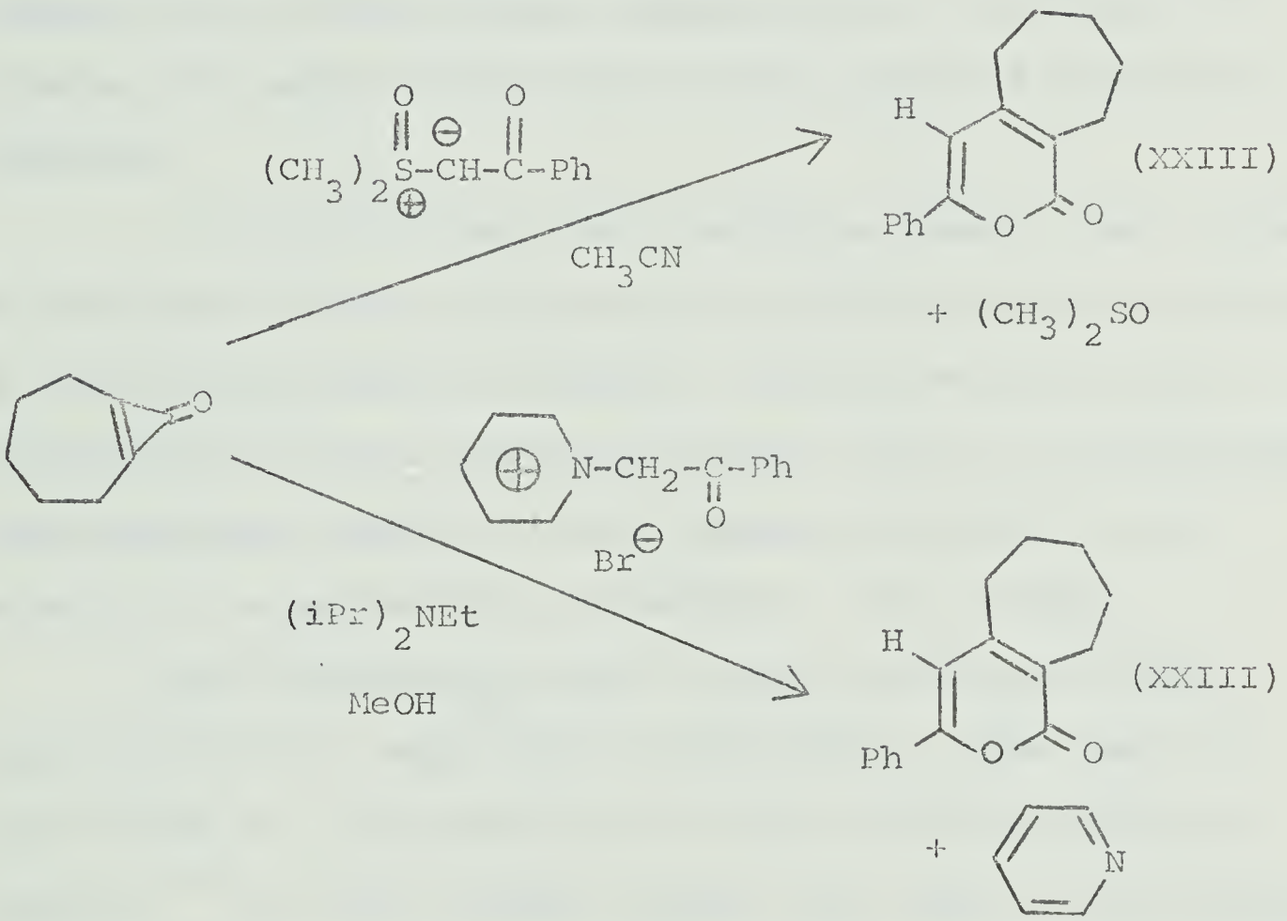
significant effect on the reactivity with 1,3-dipoles and model ylids. For this reason, cycloheptenocyclopropenone was prepared and some of its reactions with 1,3-dipoles and ylids were studied.

2. Reactions of Cycloheptenocyclopropenone with 1,3-Dipoles and Model Ylids.

When cycloheptenocyclopropenone was treated with substituted 4-oxazolines, substituted furans were obtained as was observed by analogous reactions with diphenylcyclopropenone. The following chart summarises these reactions of cycloheptenocyclopropenone which can be envisaged to proceed by an initial attack of the azomethine ylids on the carbon-carbon double bond of the cyclopropenone system, followed by decarbonylation.



Reactions have also been carried out using model ylids and again results have been obtained which parallel those given by diphenylcyclopropenone. Cycloheptenocyclopropenone reacted with dimethylsulfoxonium phenacylide, and with N-phenacylpyridinium bromide in the presence of base, to yield 3,4-cyclohepteno-6-phenyl-2-pyrone. These reactions are summarised as follows:-



In the case of the sulfoxonium ylid a much better yield of the 2-pyrone derivative was given (65.8%) than in that of the pyridinium ylid (3.6%). These results again parallel those given by diphenylcyclopropenone in that the products are formed as a consequence of an initial nucleo-

philic attack of the ylid at the carbon-oxygen bond of the cyclopropenone system.

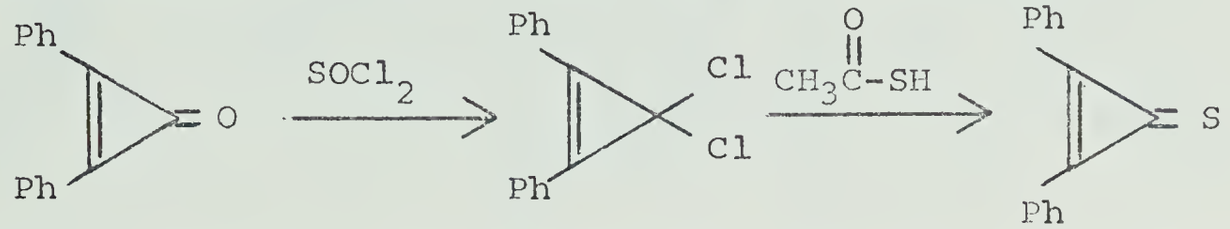
Reactions of cycloheptenocyclopropenone with diphenylisobenzofuran and with a model enamine were attempted to compare with those reactions which have been reported using diphenylcyclopropenone. Also, parallel reactions of cycloheptenocyclopropenone were attempted with azomethine ylids derived from the aziridines aforementioned. In these instances, no successfully characterised products have been isolated.

It might be concluded from these results that a loss of resonance in the cyclopropenone system results in a loss of reactivity toward 1,3-dipoles. Allied to this is the possibility that the bulky hydrocarbon chain in cycloheptenocyclopropenone, could, to some degree, sterically hinder attack by the approaching nucleophile, or 1,3-dipole.

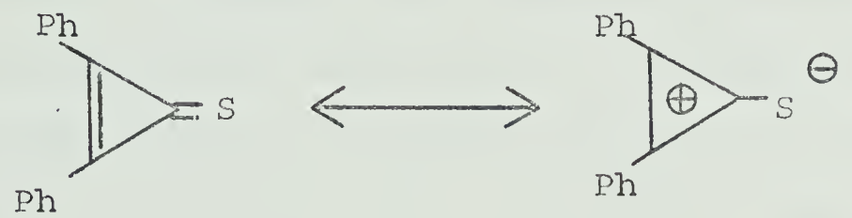
The thiocarbonyl bond is known to be more highly polarisable and a much better dipolarophile than the carbonyl bond, as illustrated by the work of Huisgen and coworkers.[39] For this reason studies were made on the reactions of diphenylcyclopropenethione with nucleophiles and with 1,3-dipoles.

3. Reactions of Diphenylcyclopropenethione.

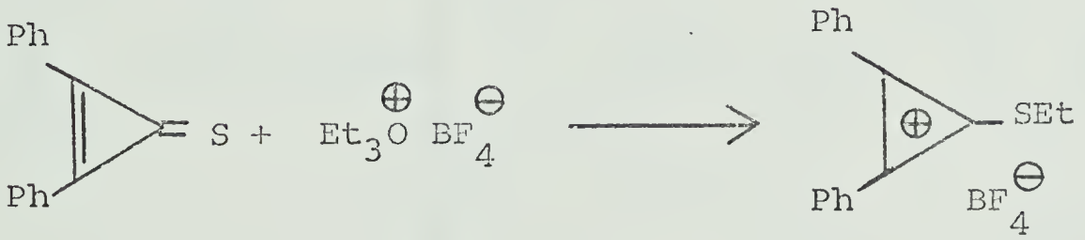
The preparation of this sulfur analogue of diphenylcyclopropenone is outlined by the following chart:-[12,14]



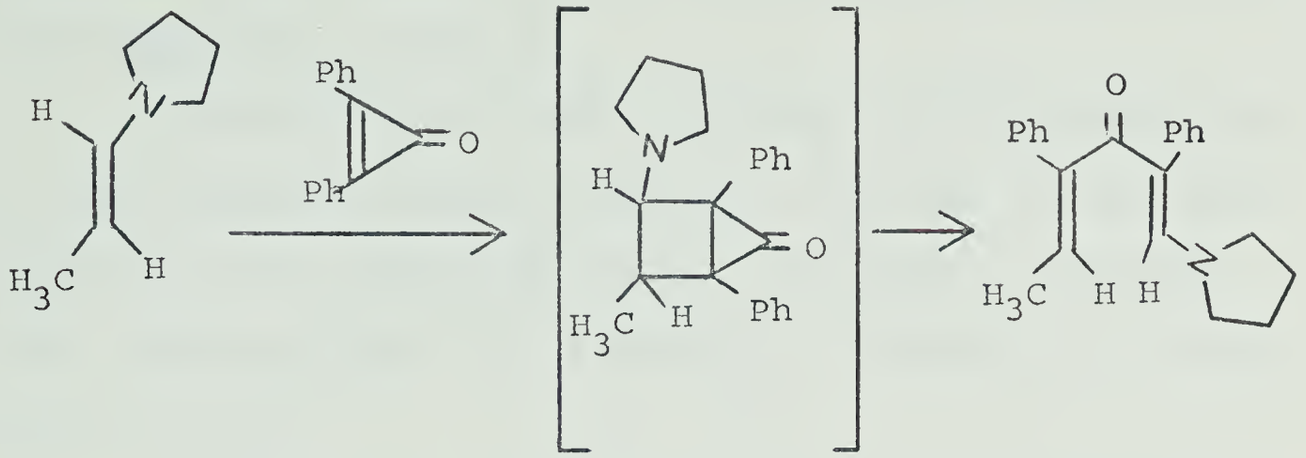
The product is a yellow crystalline solid which may be considered as a hybrid of the following resonance forms:-



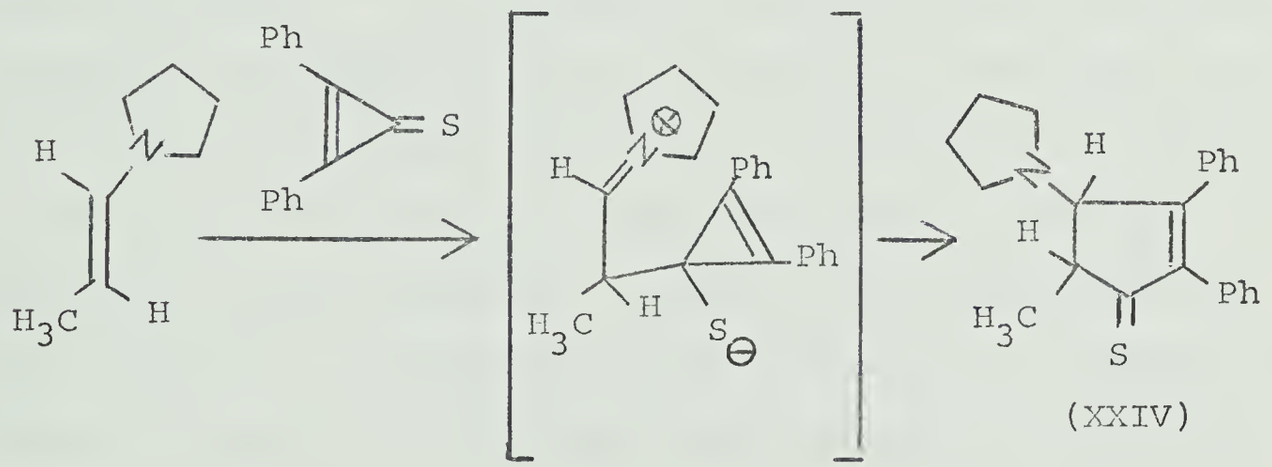
With reference to the work of Breslow and co-workers,[7] the Meerwein's salt derivative of this sulfur analogue has been prepared according to the following scheme:-



Berchtold and Ciabattoni have shown that diphenylcyclopropenone reacts with enamines, to give products which arise through initial attack at the carbon-carbon double bond.[26] For example:-



In complete contrast, reaction of the same enamine, 1-(N-pyrrolidino)-1-propene with diphenylcyclopropenethione gave a cyclopentenethione derivative, the formation of which can be explained only by an initial attack of the nucleophile at the carbon atom which carries the sulfur. This reaction is outlined as shown below:-



(XXIV)

This reaction occurred smoothly at room temperature with the evolution of heat, and the product, a white solid, was obtained in a 21.5% yield. The structure of this cyclopentenethione derivative (XXIV) was elucidated in particular by use of spin decoupling experiments in its proton magnetic

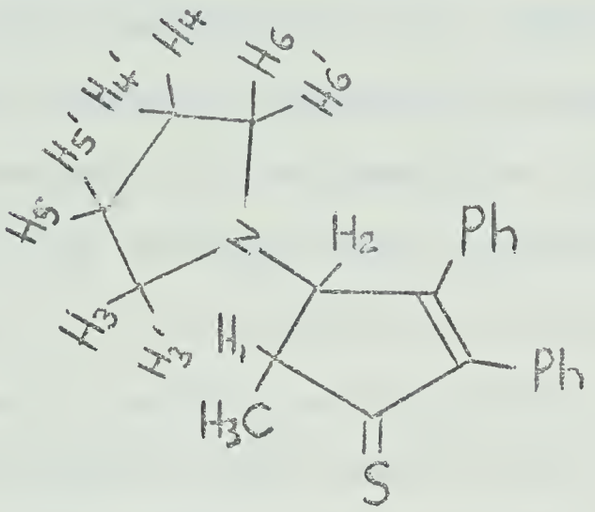
resonance. The results of the spin decoupling experiments are summarised in Table 2.

It was observed that H_6 and H_6' are not equivalent in their nuclear magnetic resonance, the same observation applying to the protons H_3 and H_3', because in agreement with structure (XXIV) the nitrogen is adjacent to an asymmetric centre.

Studies were made on the reactions of diphenylcyclopropenethione with azomethine ylids derived from substituted aziridines. 2-(p-Biphenylyl)-3-carbomethoxy-1-cyclohexylaziridine was made particularly for use in these studies, as Cromwell has reported that this aziridine undergoes relatively facile 2,3-bond scission at temperatures in the range of 65-80°.[28] In reactions attempted between this latter aziridine and diphenylcyclopropenethione no significant products were successfully identified as decomposition and/or polymerisation of the thione occurred rapidly under the conditions of the reaction. In fact, it was observed that when a solution of diphenylcyclopropenethione in benzene was allowed to stand at room temperature for about a day, the thione had decomposed completely and could not be recovered.

Eicher has shown that N-phenacylpyridinium bromide reacts with diphenylcyclopropenethione in the presence of base to give 3,4,6-triphenylthiapyrone, which is explained by an initial attack at the carbon-sulfur bond.[24] No

Table 2. Description of NMR Spectrum of Compound (XXIV) and Results of Spin-decoupling Experiments.

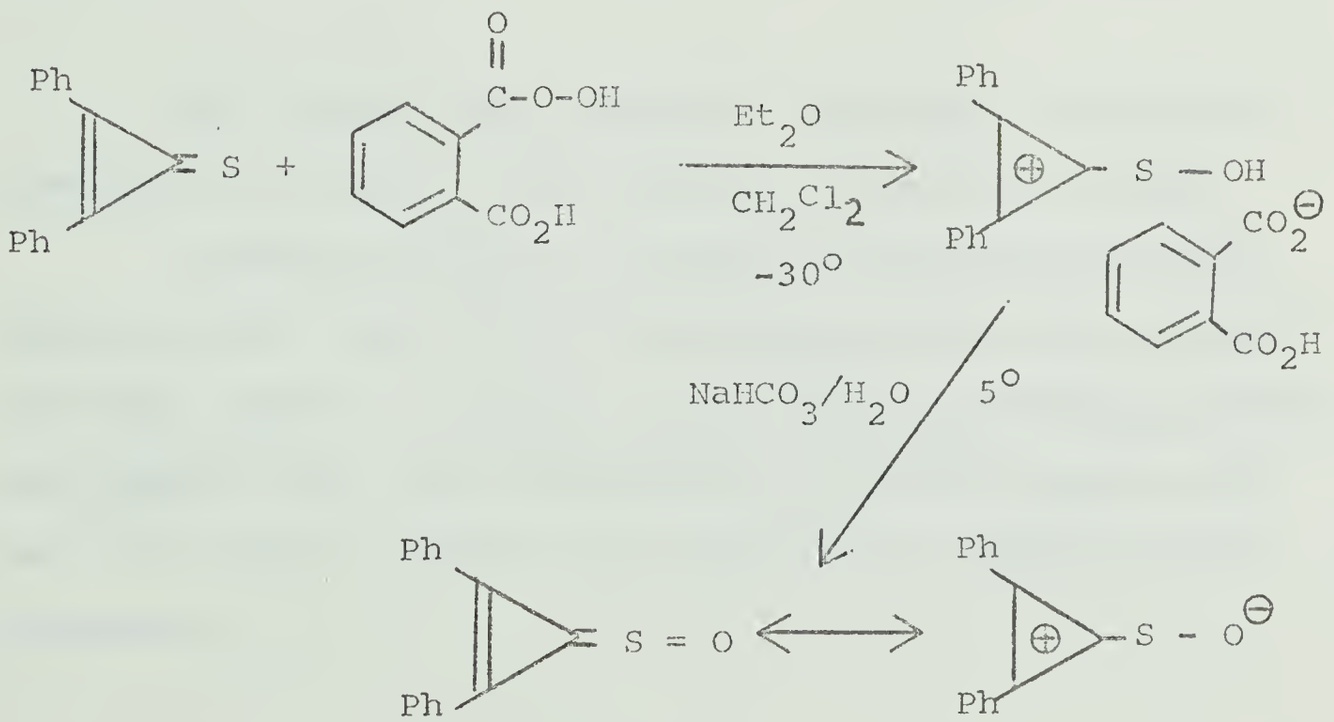


$J_{H_1-H_2} = 7$ Hz.

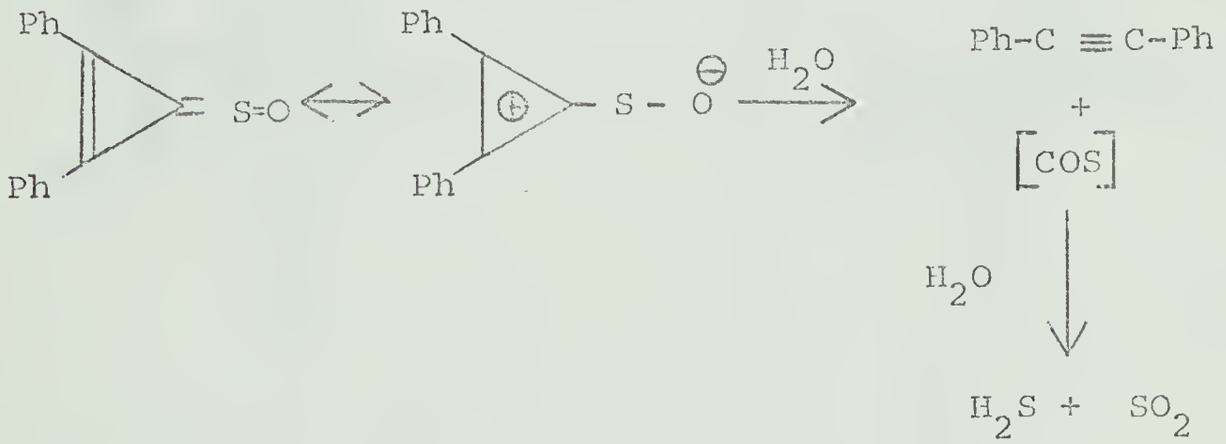
δ (downfield from TMS)	Assignment	Irradiate at:	Results
δ 1.32 doublet (3H) J=6Hz.	CH_3 protons	δ 1.32	No effect
δ 1.86-2.51 multiplet (5H)	H_{44}', H_{55}', H_1	δ 2.25	Doublet collapses at 3.17 and methyl doublet collapses to a singlet
δ 2.92-3.42 multiplet (3H)	H_3, H_6, H_2	δ 3.17	Sharpening of lines at 4.71 and increase in fine structure at 2.25
δ 4.4-5.0 multiplet (2H)	H_3', H_6'	δ 4.71	Increase in fine structure at 3.17 and at 2.25
δ 6.83-8.0 multiplet (10H)	Aromatic Protons		

instances have been reported of the reaction of an ylid, a 1,3-dipole or a nucleophile which reacts with diphenylcyclopropenethione via attack at the carbon-carbon double bond. However, a fair comparison of the reactivity of the carbon-carbon double bonds in diphenylcyclopropenone and diphenylcyclopropenethione, is not possible, since decarbonylation can occur in one instance but a comparable loss of carbon monosulfide is not energetically favourable in the other.

It was thought therefore that a study of the diphenylcyclopropenethione-S-oxide might provide a useful comparison where a loss of the elements of carbonyl sulfide would be feasible. Diphenylcyclopropenethione was oxidised to its S-oxide using monoperphthallic acid according to the following scheme:-



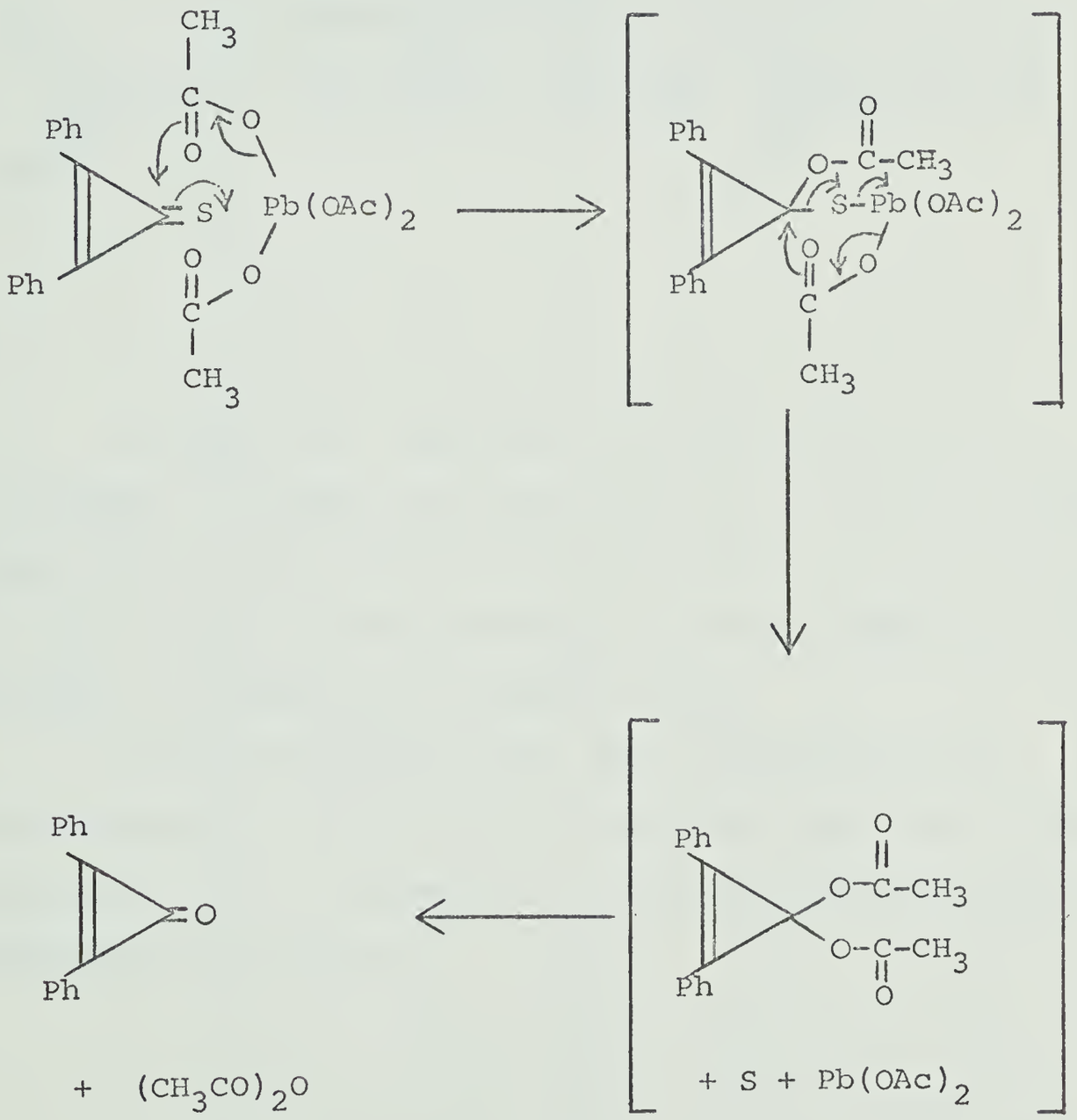
The product, an orange solid was observed to be unstable and certainly too unstable to allow any study of its reaction with 1,3-dipoles. However, in a controlled decomposition experiment of the S-oxide carried out by boiling in water, diphenylacetylene was isolated from the steam distillate in low yield and sulfur dioxide and hydrogen sulfide were tentatively recognised as products of decomposition.



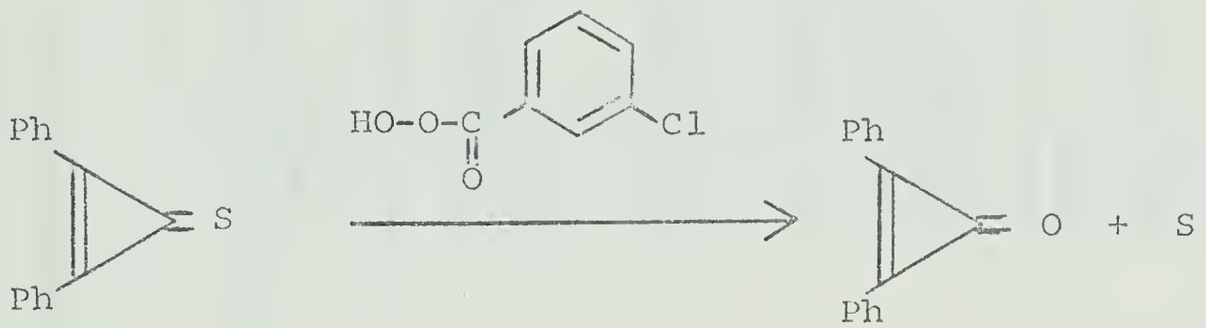
The S-oxide does decompose, therefore, as might be predicted by a loss of the elements of carbonyl sulfide.

In other attempts to prepare diphenylcyclopropenethione-S-oxide some rather surprising results were achieved which are worthy of mention. When diphenylcyclopropenethione was treated with lead tetraacetate in glacial acetic acid, the sole product isolated was identified as diphenylcyclopropenone.

This work was carried out with reference to experiments reported by Adley, Owen and Anisuzzaman who have oxidised thiocarbonates to the corresponding S-oxides using lead tetraacetate.[42] A tentative mechanism is shown below, with reference to the work of the above authors.



In a similar experiment using m-chloroperbenzoic acid as oxidant, diphenylcyclopropenone was isolated as also was elemental sulfur.



To summarise, experiments have been performed in an attempt to compare the reactivities of the carbon-carbon double bond and the carbon-heteroatom bond in cyclopropenones and derivatives, toward nucleophiles and 1,3-dipoles. The results are summarised in Tables 3 and 4.

Novel heterocycles have been prepared such as 4-oxazolines and the work has illustrated some novel synthetic procedures for the preparation of tetrasubstituted furans and derivatives of pyrrole.

Table 3. Summary of Reactions of Cyclopropenones with 1,3-Dipoles.

Reagent	Substrate	Site of Attack	Product Type	Reference
2-Aryl-3-carbo-alkoxy-substituted aziridines	DPP	C=C	Derivatives of 2,3-dihydropyr-role	*
2-Aryl-3-acyl or aroyl substituted aziridines	DPP	C=O	Substituted 4-oxazolines	* 23
Diazomethane	DPP	C=C	4-pyridazone	22
Diphenylisobenzo-furan	DPP	C=O	Substituted benzocyclo-heptenone	41
Substituted 4-oxa-zolines	DPP	C=C	Substituted furans	*, 23 35,36
Substituted 4-oxa-zolines	CCP	C=C	Substituted furans	*

LEGEND - * - As described in this thesis
DPP - Diphenylcyclopropenone
CCP - Cycloheptenocyclopropenone

Table 4. Summary of Reactions of Cyclopropenones with Nucleophiles.

Reagent	Substrate	Site of Attack	Product Type	Ref.
Hydroxide ion	DPP	C=O	cis-2-phenylcinnamic acid	7
Hydroxide ion	CCP	C=O	Cycloheptene-1-carboxylic acid	15
Alkoxide ion	DPP	C=O	α,β unsatd. ester	15
	CCP	C=O	α,β unsatd. ester	15
N-Phenacyl Pyridinium bromide/base	DPP	C=O	2-pyrone deriv.	24
	CCP	C=O	2-pyrone deriv.	*
	DPPTH	C=S	2-thiapyran deriv.	24
Trimethyl ammonium phenacylide	DPP	C=O	2-pyrone deriv.	41
Dimethylsulfoxonium phenacylide	DPP	C=O	2-pyrone deriv.	41
	CCP	C=O	2-pyrone deriv.	*
Enamine e.g. 1-(N-pyrrolidino-1-propene	DPP	C=C	deriv. of hexadienone	26
	DPPTH	C=S	deriv. of cyclopentene-thione	*

continued overleaf

Table 4. Continued

Reagent	Substrate	Site of Attack	Product Type	Ref.
Hydrogen Peroxide	DPP	C=C	desoxybenzoin	60
Hydroxylamine	DPP	C=C	3,4-diphenylisoxazolone, desoxybenzoin oxime	7
Diethylamine	DPP	C=O	N,N-Diethyl-α-phenylcinnamic acid amide	58
Malononitrile Anion	DPP	C=O	Methylenecyclopropene	17
Ynamine	DPP	C=O	Cyclopentanedione	59
Grignard Reagent	DPP	C=O	Dicyclopropenyl ether	7
Phenyl Lithium	DPP	C=C	Carboxylic Acid	25

LEGEND * - As described in this thesis

DPP - Diphenylcyclopropenone

CCP - Cycloheptenocyclopropenone

DPPTH - Diphenylcyclopropenonethione

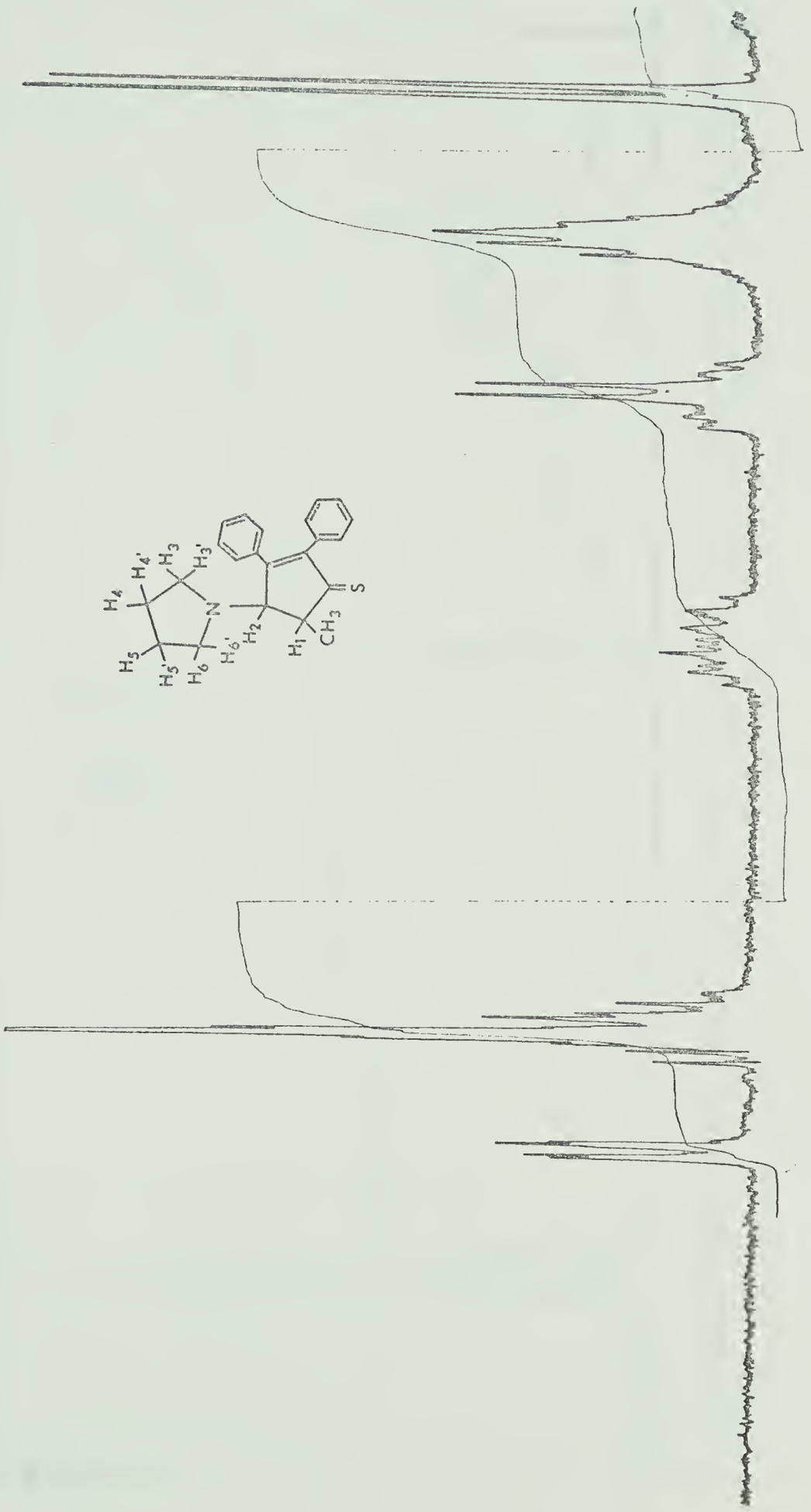


Figure 1. NMR Spectrum of Compound (XXIV)

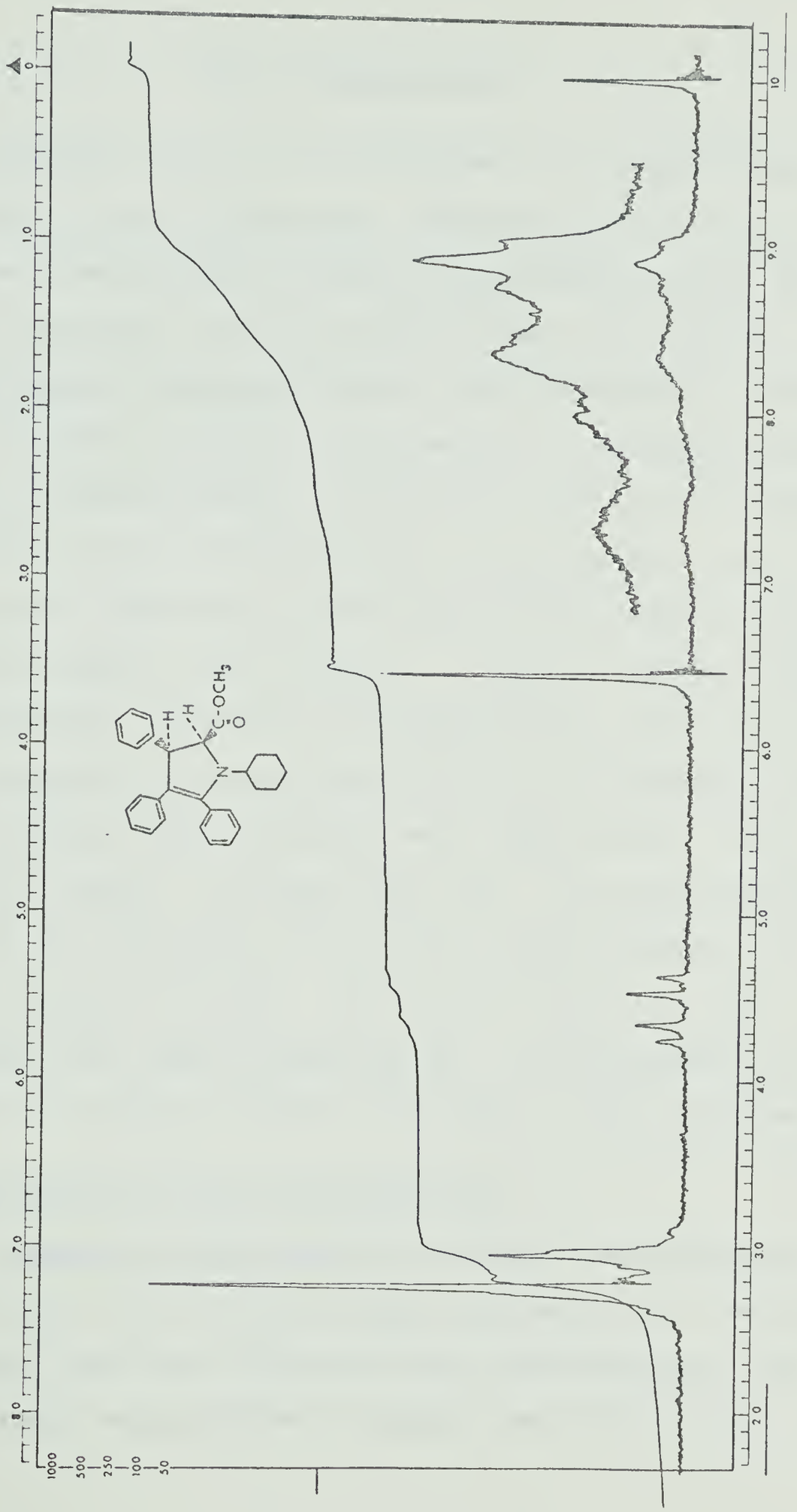


Figure 2. NMR Spectrum of Compound (VIII)

III. EXPERIMENTAL

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer model 421 spectrophotometer, and only the principal, sharply defined peaks are reported. Nuclear magnetic resonance spectra were recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on approximately 10-15% (w/v) solutions in deuterochloroform, with tetramethylsilane as a standard. Line positions are reported in parts per million from the reference. Absorption spectra were recorded in 'spectro'-grade solvents on a Beckman DB recording spectrophotometer. Mass spectra were determined on an Associated Electrical Industries MS-9 double focusing high resolution mass spectrometer. The ionization energy, in general was 70eV. Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15,000. BDH basic alumina was used for thin layer and column chromatography. Micro-analyses were carried out by Mrs. D. Mahlow and staff, of this Department.

1. Preparation of the Cyclopropenones.

Diphenylcyclopropenone was prepared according to the procedure described by Breslow, Eicher, Krebs, Peterson and Posner[7] with the following slight modification. The crude product was purified by Soxhlet extraction using

cyclohexane as solvent. Diphenylcyclopropenone crystallised from cyclohexane as white needles, m.p. 123-124° (lit. m.p., 119-120°).

Cycloheptenocyclopropenone was prepared according to the method of Breslow and co-workers.[8] The product crystallised from pentane-hexane as a white solid (m.p. 50.5-51.5°) (lit. m.p. 52-53°).

Diphenylcyclopropenethione was prepared according to the method of Eicher and Frenzel.[14]

To a solution of diphenylcyclopropenone (2.06 g., 0.01 mole) in dry cyclohexane (10 ml.), was added thionyl chloride (2 ml.) and the resultant solution was heated on a steam bath for 15 min. The solvent and unreacted thionyl chloride were removed by distillation and the solid residue was redissolved in dry cyclohexane (12 ml.). To this solution, was added by dropwise addition, a solution of thioacetic acid (1.67 g., 0.022 mole) in dry cyclohexane (4 ml.), the temperature being maintained at 35-40°. The resultant yellow solid product was recrystallised from cyclohexane (80 ml.), as deep yellow plates (1.1 g., 50% based on diphenylcyclopropenone) m.p. 122° (lit., m.p. 118.5-119.5°).

NMR spectrum: δ 7.36-8.3 multiplet (aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1350 cm^{-1} (C=S).

Mass Spectrum: m/e 222.

Calcd. for $C_{15}H_{10}S$: 222.0503

Found: 222.0502

Anal. Calcd. for $C_{15}H_{10}S$: C,81.09; H,4.50; S, 14.41.

Found: C,81.05; H,4.51; S, 14.39.

2. Synthesis of the Aziridines.

2-(p-Biphenylyl)-1-cyclohexyl-substituted aziridines were prepared by the following general method. Condensation of biphenyl-4-aldehyde with the appropriate active methylene compound, afforded the corresponding α,β -unsaturated carbonyl compound. Bromination in chloroform solution, followed by treatment of the dibromo derivative with cyclohexylamine in benzene solution, yielded the desired aziridine.

Biphenyl-4-aldehyde was prepared according to the procedure described by Cromwell and Cahoy.[27] The product crystallised from methanol as a white solid (59%) m.p. 57-58° (lit., m.p. 58-59°).

3-Benzoyl-2-(p-biphenylyl)-1-cyclohexylaziridine (I).

4-Phenylstyryl phenyl ketone was prepared using the Kohler-Chadwell method for the preparation of phenyl styryl ketone.[43] The product was recrystallised from methanol as a yellow solid (53%) m.p. 110.5-112° (lit., m.p. 111.5-112.5°).[44]

3-(p-Biphenylyl)-2,3-dibromo-1-phenylpropanone. To a solution of 4-phenylstyryl phenyl ketone (22 g., 0.0775 mole) in chloroform (100 ml.), was added during 20 min. with

stirring, a solution of bromine (12.4 g., 0.0775 mole) in chloroform (50 ml.). The bromine colour was discharged very rapidly and after the addition was completed, the resultant pale yellow solution was stirred for 15 min. The solvent was removed by distillation under reduced pressure, leaving the product as a pale yellow solid (34.2 g., 100%). It was purified by recrystallisation from benzene-hexane to yield a white solid (m.p. 185.5-186°).

NMR spectrum: AB quartet, centred at δ5.7 and 6.0, J_{A-B} 11 Hz., (2H); multiplet δ7.25-8.3 (14H).

IR spectrum: $CHCl_3$ ν_{max} 1690 cm^{-1} (aromatic C=O).

Anal. Calcd. for $C_{21}H_{16}Br_2O$: C, 56.75; H, 3.63; Br, 35.99.

Found: C, 56.66; H, 3.56; Br, 36.22.

3-Benzoyl-2-(p-biphenylyl)-1-cyclohexylaziridine. (I)

To a solution of 3-p-biphenylyl-2,3-dibromo-1-phenylpropanone (22.2 g., 0.05 mole) in benzene (300 ml.), was added cyclohexylamine (54.5 g., 0.55 mole) and the mixture was stirred at room temperature for 24 hr. The cyclohexylamine hydrobromide which had separated, was removed by filtration, the filtrate was ashed with water (2 x 100 ml.) and dried ($MgSO_4$). The benzene and most of the excess cyclohexylamine were removed by careful distillation under reduced pressure to leave a pale yellow oil (20 g., 100%), which when triturated

under hexane gave the desired aziridine as a white solid (m.p. 107-110°). Recrystallisation from methanol afforded a cis/trans mixture of the product (m.p. 127°).

NMR spectrum: Multiplet δ 1.0-3.0 (11H, cyclohexyl protons); singlet δ3.23, singlet δ3.63 (2H); multiplet δ7.2-8.3 (14H, aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1680 cm^{-1} (aromatic C=O).

Mass spectrum: Calcd. for $C_{27}H_{27}NO$: 381.2094

Found: 381.1974

Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.00; H, 7.14; N, 3.67.

Found: C, 84.90; H, 7.23; N, 3.64.

3-Acetyl-2-(p-biphenylyl)-1-cyclohexylaziridine (II) was synthesised according to the method of Cromwell and Cahoy.[27] Recrystallisation from ether afforded a cis/trans mixture of the product (65%) (m.p. 84-89°). (lit. m.p. two isomers, 82-83° and 102-103°).

2-(p-Biphenylyl)-3-carbomethoxy-1-cyclohexylaziridine (III) was synthesised according to the method of Woller and Cromwell.[28] The desired aziridine was purified by recrystallisation from hexane as a white solid (97%) m.p. 69-72° and used in subsequent reactions as a cis/trans mixture.

3-Carboalkoxy-1-cyclohexyl-2-phenyl-substituted aziridines were synthesised from the appropriate cinnamic acid esters.

3-Carboisopropoxy-1-cyclohexyl-2-phenylaziridine. (VI)

Isopropyl Cinnamate was prepared by the Fischer-Speier procedure, using sulfuric acid as catalyst. The product was obtained as a colourless, sweet-smelling liquid (62%) b.p. 109-110°/4mm. (lit., b.p. 107.5-108°/2mm.).[45]

Isopropyl 2,3-dibromo-3-phenyl propionate. Isopropyl cinnamate (9.5 g., 0.05 mole) was dissolved in chloroform (100 ml.) and a solution of bromine (8 g., 0.05 mole) in chloroform (50 ml.) was added by dropwise addition with stirring, over 45 min. The resultant solution was stirred for a further 3 hr. and then evaporated *in vacuo* to yield the crude dibromide (17.3 g., 100%) as a colourless oil. This oil, which slowly crystallised upon cooling, was purified by recrystallisation from hexane, as a white solid, m.p. 52.5-53°.

NMR spectrum: Doublet δ1.33 J=6Hz. (6H); AB quartet centred at: δ4.76, δ5.29 J=12Hz. (2H); Multiplet δ4.93-5.4 (1H); Singlet δ7.33 (5H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1730 cm^{-1} (C=O)

Anal. Calcd. for $C_{12}H_{14}Br_2O_2$: C, 41.16; H, 4.03; Br, 45.67.
Found: C, 41.10; H, 3.99; Br, 45.49.

3-Carboisopropoxy-1-cyclohexyl-2-phenylaziridine. (VI)

To a solution of isopropyl 2,3-dibromo-3-phenyl propionate (7g., 0.02 mole) in benzene (100 ml.), was added cyclohexylamine (21.8 g., 0.22 mole) and the mixture was stirred at room temperature for 24 hr. The cyclohexylamine hydrobromide which had separated was removed by filtration, the filtrate was washed with water (2 x 50 ml.) and dried ($MgSO_4$). The solvent and most of the excess cyclohexylamine were removed by careful distillation under reduced pressure, ensuring that the temperature in the distillation vessel did not exceed 50°. This left the crude aziridine as a yellow oil, which was purified by chromatography on BDH basic alumina using benzene as eluent. The desired aziridine was thus isolated as a pale yellow oil (5.2 g., 92.2%) and as a mixture of cis and trans isomers.

NMR spectrum: Multiplet δ0.66-2.0 (10H); two doublets δ0.93 and δ1.26 J=12Hz. (6H) (methyl protons of isopropyl group in cis and trans isomers); multiplet δ2.25-3.3 (3H) (proton in cyclohexyl ring, adjacent to nitrogen and 2 protons in aziridine ring); septet δ4.55-5.20 (1H); multiplet δ7.0-7.6 (5H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1710 cm^{-1}, shoulder 1730 cm^{-1} (C=O in cis and trans isomers).

Mass spectrum: m/e 287.

Calcd. for $C_{18}H_{25}NO_2$: 287.1885

Found: 287.1881

Anal. Calcd. for $C_{18}H_{25}NO_2$: C, 75.21; H, 8.77; N, 4.87.

Found: C, 74.62; H, 8.90; N, 5.05.

3-Carbomethoxy-1-cyclohexyl-2-phenylaziridine. (IV)

Methyl 2,3-dibromo-3-phenyl propionate was prepared by bromination of methyl cinnamate, by an exactly analogous procedure to that previously described for the isopropyl ester. The crude product, a pale yellow solid, was recrystallised from 98% ethanol as a white solid (87.3% after recrystallisation) m.p. 118-119° (lit., m.p. 117°).[46]

The desired aziridine was then prepared and purified by an exactly similar procedure to that previously described for the corresponding isopropyl ester aziridine. The product, a pale yellow oil (95%) was isolated as a mixture of cis/trans isomers.

NMR spectrum: Multiplet δ0.9-2.1 (10H); multiplet δ2.35-3.3 (3H); singlets δ3.45 and δ3.75 (3H) (methyl protons of ester in cis and trans isomers); multiplet δ7.0-7.7 (5H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1725 cm^{-1}, shoulder 1740 cm^{-1}

Mass spectrum: Calcd. for $C_{16}H_{21}NO_2$: 259.1572

Found: 259.1568

Anal. Calcd. for $C_{16}H_{21}NO_2$: C, 74.08; H, 8.17; N, 5.40.
Found: C, 75.12; H, 8.22; N, 5.59.

3-Carboethoxy-1-cyclohexyl-2-phenylaziridine. (V)

Ethyl 2,3-dibromo-3-phenylpropionate was prepared by bromination of ethyl cinnamate, by a procedure as described previously for the corresponding isopropyl ester analogue. The crude dibromide, a pale yellow solid, was purified by recrystallisation from hexane to yield the white crystalline dibromide (91.6%) m.p. 76-76.5° (lit., m.p. 75-76°).[47]

The 3-carboethoxy substituted aziridine was then prepared from the dibromide and purified, by an exactly analogous procedure to that previously described for the other aziridines in this series. The product was isolated as a mixture of cis/trans isomers in the form of a pale yellow oil (73.6%).

NMR spectrum: Multiplet δ 0.7-2.0 (13H) (10H of cyclohexyl ring and methyl protons of ester); multiplet 2.35-3.35 (3H). Pair of doublets 4.10 and 4.35 J=7Hz., (CH_2 of ester group); multiplet 7.20-8.0 (5H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1715 cm^{-1} and 1738 cm^{-1}. (C=O)

Mass spectrum: m/e 273.

Calcd. for $C_{17}H_{23}NO_2$: 273.1729
Found: 273.1728

Anal. Calcd. for $C_{17}H_{23}NO_2$: N, 5.12.

Found: N, 4.88.

Attempted Synthesis of 3-Carbophenoxy-1-cyclohexyl-2-phenylaziridine. This synthesis was attempted, without success, in the same manner as previously described for the 3-carboalkoxy-substituted aziridines. The final product of the reaction was successfully identified as 2-bromo-N-cyclohexyl-3-phenyl-propenoic acid amide.

Phenyl cinnamate was prepared as described by the procedure described by Vogel.[48] The crude product was purified by distillation under reduced pressure b.p. 190-210°/15-20 mm., (lit., b.p. 190-210°/15 mm.) and finally by recrystallisation from ethanol as a white crystalline solid (78%) m.p. 70-71° (lit., m.p. 75-76°).

Phenyl 2,3-dibromo-3-phenyl propionate was prepared by bromination of phenyl cinnamate, by an analogous procedure previously described for the bromination of the alkyl esters of cinnamic acid. The crude product (100%) was purified by recrystallisation from benzene-hexane as a white crystalline solid m.p. 130.5° (lit., m.p. 127°).[49]

2-Bromo-N-cyclohexyl-3-phenyl propenoic acid amide. To a solution of phenyl 2,3-dibromo-3-phenylpropionate (7.7 g., 0.02 mole) in benzene (150 ml.), was added cyclohexylamine (21.8 g., 0.22 mole) and the resultant mixture was stirred for 24 hr. The cyclohexylamine hydrobromide which had

separated was removed by filtration and the filtrate was washed with water (2 x 100 ml.) and dried ($MgSO_4$). The benzene and excess base were removed by evaporation *in vacuo* and trituration of the residue with a small volume of hexane afforded the bromo-amide derivative as a white solid (5 g., 82.3%) m.p. 95-97°. Purification was achieved by recrystallisation from hexane yielding the pure product m.p. 100-101°.

NMR spectrum: δ0.7-2.25 multiplet (10H) (cyclohexyl protons); δ3.55-4.2 multiplet (1H) (C-H of cyclohexyl ring adjacent to nitrogen); δ6.55-6.95 multiplet (1H) (N-H); δ7.22-7.92 (5H) (aromatic protons); δ8.33 singlet (1H) (vinyl proton).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1650 cm^{-1} (α,β-unsatd. C=O of amide) 3408 cm^{-1} (-NH stretch).

Mass spectrum: Calcd. for $C_{15}H_{18}Br^{79}NO$: 307.0570
Found: 307.0571

Anal. Calcd. for $C_{15}H_{18}BrNO$: C, 58.42; H, 5.89; N, 4.54.
Found: C, 58.49; H, 5.95; N, 4.80.

A similar experiment carried out, using 3 molar equivalents of cyclohexylamine rather than 11 molar equivalents, gave the same product (67.4%). Phenol, a by-product of this reaction, was also isolated (62.3%) and characterised by comparison with an authentic sample. Isolation of the phenol was simply achieved by extraction of the benzene solution (after

removal of cyclohexylamine hydrobromide) with cold 0.1 M sodium hydroxide solution. Acidification of this extract, followed by extraction with ether, readily afforded the phenol.

3. Reactions of Aziridines with Diphenylcyclopropenone.

4-Oxazolines

4-Benzoyl-2-(p-biphenylyl)-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-oxazoline. (XIII)

A solution of diphenylcyclopropenone (1.03 g., 0.005 mole) and 3-benzoyl-2-(p-biphenylyl)-1-cyclohexylaziridine (2.54 g., 0.0067 mole) in benzene (40 ml.) was heated under reflux for 20 hr. The solution assumed a pink colouration after boiling for 15 min. and very soon became very deep red in colour. The solvent was evaporated *in vacuo* leaving a deep red gum from which the desired oxazoline was isolated, by chromatography on BDH basic alumina using benzene as eluent. The 4-oxazoline eluted as a broad yellow band, which, after removal of the benzene, followed by trituration of the residue with ethanol, afforded the product as a pink solid (2.93 g., 100%). Crystallisation of this material was found not to be possible as even gentle heat transformed the 4-oxazoline to a red gummy solid or solution in both polar and relatively non-polar solvents. Further purification was achieved by re-chromatographic techniques on basic alumina yielding a pink solid m.p. 122-123° (deep red melt).

NMR spectrum: δ 0.4-2.0 multiplet (10H, cyclohexyl protons); δ 2.5-3.3 multiplet (1H); δ 5.1 singlet (1H, benzylic proton); δ 6.7-8.3 broad multiplet (25H, aromatic protons and vinyl proton).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1700 cm^{-1} (aromatic C=O).

Mass spectrum: No molecular ion shown. Species of highest molecular weight corresponds to M-(biphenyl-4-aldehyde, cyclohexylamine anil) i.e. m/e (587-263) = m/e 324.

Calcd. for $C_{23}H_{16}O_2$: 324.1147

Found: 324.1150

Strong peak at m/e 263.

Anal. Calcd. for $C_{42}H_{37}NO_2$: C, 85.82; H, 6.35; N, 2.38.

Found: C, 85.64; H, 6.28; N, 2.32.

4-Acetyl-2-(p-biphenylyl)-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-oxazoline. (XIV)

A solution of diphenylcyclopropenone (0.206 g., 0.001 mole) and 3-acetyl-2-(p-biphenylyl)-1-cyclohexylaziridine (0.424 g., 0.00133 mole) in benzene (15 ml.), was heated under reflux for 24 hr. At the end of the reaction period, the solution was red in colour. The solvent was removed in vacuo, and the red gum which remained was purified by chromatography on BDH basic alumina using benzene as eluent. Removal of the benzene and trituration of the residue with a small volume of ethanol gave the desired 4-oxazoline as a white solid

(0.310 g., 59%) m.p. 136-137° (red melt). This product slowly cyrstallised from ethanol as a white crystalline solid which slowly turned pink on exposure to light m.p. 141-142° (red melt).

NMR spectrum: δ0.6-2.1 multiplet (10H, cyclohexyl protons); δ1.9 singlet (3H, methyl protons); δ2.73-3.5 multiplet (1H); δ4.86 singlet (1H, benzylic proton); δ6.65-8.10 multiplet (20H, aromatic protons and vinyl proton).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1700 cm^{-1} (α,β-unsatd. C=O)

Mass spectrum: Calcd. for $C_{37}H_{35}NO_2$: 525.2668

Found: 525.2675

Major fragmentation shows principal peaks at m/e 262, 263.

Anal. Calcd. for $C_{37}H_{35}NO_2$: C, 84.53; H, 6.72; N, 2.67.

Found: C, 84.32; H, 6.68; N, 2.58.

4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline. (XV)

This material was prepared according to the procedure of Lown, Smalley and Dallas,[23] with one slight modification. Instead of reacting equimolar proportions of starting materials, diphenylcyclopropenone (1 molar equiv.) was treated with the 3-benzoyl substituted aziridine (1.33 molar equiv.). The result of this was to increase the yield (57%) to that reported (46.5%).

2,3-Diphydropyrroles.

5-(p-Biphenylyl)-2-carbomethoxy-1-cyclohexyl-2,3-dihydro-3,4-diphenylpyrrole. (VII)

A solution of diphenylcyclopropenone (1.03 g., 0.005 mole) and 2-(p-biphenylyl)-3-carbomethyoxy-1-cyclohexylaziridine (1.675 g., 0.005 mole) in benzene (40 ml.), was heated under reflux for 20 hr. Removal of the solvent *in vacuo*, followed by trituration of the residual orange oil with a small volume of heptane, gave the crude dihydropyrrole as a yellow solid (1.38 g., 51%). Purification of the crude product was achieved by recrystallisation from ethanol to yield the pure product m.p. 174°.

NMR spectrum: δ0.75-2.90 broad multiplet (11H, cyclohexyl protons); δ3.57 singlet (3H, methyl protons); AB quartet, centred at δ5.41 and δ5.70 J=6Hz. (2H, attached to pyrrole ring); δ6.90-7.70 multiplet (19 H, aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1725 cm^{-1} (C=O of an ester).

Mass spectrum: Base peak at M-2 (dehydrogenation under conditions of mass spectrometry).

Calcd. for $C_{36}H_{33}NO_2$: 511.2511

Found: 511.2510

Anal. Calcd. for $C_{36}H_{35}NO_2$: C, 84.16; H, 6.87; N, 2.73.

Found: C, 84.01; H, 6.74; N, 2.83.

A similar experiment was carried out using diphenylacetylene instead of diphenylcyclopropenone, but after heating under reflux for 20 hr., the diphenylacetylene was recovered unchanged. However by using a higher boiling solvent, namely toluene, and a more prolonged period of heating, the desired 2,3-dihydropyrrole was isolated, in low yield.

A solution of diphenylacetylene (0.356 g., 0.002 mole) and 2-(p-biphenylyl)-3-carbomethoxy-1-cyclohexylaziridine (0.67 g., 0.002 mole) in toluene (16 ml.) was heated under reflux for 89 hr. The solvent was evaporated *in vacuo* and the residual gum was dissolved in heptane and the resultant solution cooled overnight in the refrigerator. The solid which had separated was collected and recrystallised from ethanol (0.016 g., 1.6%) m.p. 174°. This product was identical (undepressed mixed m.p. and superposable IR spectrum to that pyrrole derivative (VII) given by reaction of the named aziridine with diphenylcyclopropenone.

2-Carbomethoxy-1-cyclohexyl-2,3-dihydro-3,4,5-triphenylpyrrole. (VIII)

A solution of diphenylcyclopropenone (1.03 g., 0.005 mole) and 3-carbomethoxy-1-cyclohexyl-2-phenylaziridine (1.3 g., 0.005 mole) in toluene (20 ml.) was heated under reflux for 20 hr. The solvent was evaporated *in vacuo* and the residual gum was triturated with a small volume of hexane to

yield the product (2 g., 85.8%) as a pale yellow solid. Recrystallisation from ethanol afforded the pure 2,3-dihydropyrrole as a white crystalline solid m.p. 149.5-150°.

NMR spectrum: δ0.8-2.3 multiplet (10H, cyclohexyl protons); 2.42-3.0 multiplet (1H); δ3.57 singlet (3H); AB quartet, centred at δ5.43 and δ5.70 (2H) J=6Hz.; δ6.83-7.5 multiplet (15H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1725 cm^{-1} (C=O of an ester).

Mass spectrum: m/e (M-2) observed as the base peak.

Calcd. for $C_{30}H_{29}NO_2$: 437.2355.

Found: 437.2350.

Anal. Calcd. for $C_{30}H_{31}NO_2$: C, 82.33; H, 7.15; N, 3.20.

Found: C, 82.37; H, 7.11; N, 3.50.

A similar experiment carried out with diphenylcyclopropenone, using benzene as solvent, gave only 9.9% of the desired 2,3-dihydropyrrole derivative. From this experiment, diphenylcyclopropenone was recovered (68%).

A solution of diphenylacetylene (0.9 g., 0.005 mole) and 3-carbomethoxy-1-cyclohexyl-2-phenylaziridine (1.3 g., 0.005 mole) in toluene (15 ml.) was heated under reflux for 5 days. The toluene was evaporated in vacuo and the residual gum was purified by chromatography on basic alumina, using benzene as eluent. A yellow band was eluted first, which after removal of the solvent and trituration of the residue

with a small volume of hexane gave the 2,3-dihydropyrrole derivative as a yellow solid (0.582 g., 26.5%). Recrystallisation from ethanol afforded the white solid product m.p. 148-149° which was identical in all respects (undepressed mixed m.p. and superposable IR spectrum) to that product (VIII) described above.

2-Carboethoxy-1-cyclohexyl-2,3-dihydro-3,4,5-triphenylpyrrole. (IX)

A solution of diphenylcyclopropenone (0.687 g., 0.0033 mole) and 3-carboethoxy-1-cyclohexyl-2-phenylaziridine (0.910 g., 0.0033 mole) in toluene (20 ml.), was heated under reflux for 14 hrs. The solvent was removed in vacuo and the residual orange oil was triturated with a small volume of hexane to yield the crude 2,3-dihydropyrrole derivative (0.872 g., 52.2%), as a pale yellow solid m.p. 109-111°. Recrystallisation from ethanol afforded the pure derivative m.p. 115-116°.

NMR spectrum: δ0.7-2.2 multiplet (13H, cyclohexyl protons and protons of $C\underline{H}_3$ group of ester); δ2.4-3.0 multiplet (1H, C-$\underline{H}$ of cyclohexyl adjacent to nitrogen); δ4.03 doublet of doublets J=7Hz., (2H, -$C\underline{H}_2$ group of ester); AB quartet centred at δ5.37 and δ5.67 (2H, protons attached to pyrrole ring) J=6Hz. δ6.8-7.46 (15H, aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1717 cm^{-1} (C=O of ester).

Mass spectrum: m/e (M-2)

Calcd. for $C_{31}H_{31}NO_2$: 449.2362

Found: 449.2355

Anal. Calcd. for $C_{31}H_{33}NO_2$: C, 82.41; H, 7.37; N, 3.10.

Found: C, 82.69; H, 7.53; N, 3.01.

2-Carboisopropoxy-1-cyclohexyl-2,3-dihydro-3,4,5-triphenylpyrrole. (X)

A solution of diphenylcyclopropenone (1.03 g., 0.005 mole) and 3-carboisopropoxy-1-cyclohexyl-2-phenylaziridine (1.44 g., 0.005 mole), in o-xylene (40 ml.), was heated under reflux for 16 hr. The solvent was removed by distillation under reduced pressure, and the resultant orange gum crystallised upon cooling. The crude product, a yellow solid (0.952 g., 40.9%) was collected, washed with a small volume of hexane and purified by recrystallisation from ethanol m.p. 122-123°.

NMR spectrum: δ0.67-2.3 multiplet (16H); δ2.4-3.0 multiplet (1H); δ4.52-5.2 multiplet (1H, C-H of isopropyl group); AB quartet, centred at δ5.36 and δ5.67 (2H) J=6Hz., δ6.7-7.5 Multiplet (15H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1710 cm^{-1} (C=O).

Mass spectrum: m/e (M-2)

Calcd. for $C_{32}H_{33}NO_2$: 463.2511

Found: 463.2512.

Anal. Calcd. for $C_{32}H_{35}NO_2$: C, 82.49; H, 7.58; N, 3.01.

Found: C, 82.49; H, 7.62; N, 2.82.

A similar experiment carried out in toluene gave as a result, unchanged diphenylcyclopropenone (46.5% recovery). Hence o-xylene, a higher boiling solvent, was used in the place of toluene.

4. Derivatives Prepared to Support the Proposed 4-Oxazoline Structures.

4-Acetyl-2-(p-biphenylyl)-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-oxazoline. (XIV)

Reaction with diphenylcyclopropenone

A solution of diphenylcyclopropenone (0.103 g., 0.0005 mole) and the 4-oxazoline (0.263 g., 0.0005 mole) in o-xylene (20 ml.), was heated under reflux for 18 hr. The solvent was evaporated *in vacuo* and the residual dark red gum was purified by chromatography on basic alumina using benzene as eluent. A yellow band was eluted which, when the solvent was removed *in vacuo* gave a yellow oil. Trituration of this residual oil with a small volume of hexane afforded 4-acetyl-5-(cis-1,2-diphenyl vinyl)-2,3-diphenylfuran (XX) (0.098 g., 44.5%), m.p. 162-165°. This yellow product was purified by recrystallisation from ethanol containing a trace of water, as bright yellow crystals m.p. 169-170°.

NMR spectrum: δ 1.72 singlet (3H, $-CH_3$ protons); δ 6.6-7.9 multiplet (21H, aromatic protons and vinyl proton).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1690 cm^{-1} (conjugated, α,β-unsatd. C=O).

Mass spectrum: m/e 440

Calcd. for $C_{32}H_{24}O_2$: 440.1776

Found: 440.1774

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.22; H, 5.49.

Found: C, 87.18; H, 5.54.

Reaction with Dimethylfumarate.

A solution of the 4-acetyl-4-oxazoline (0.263 g., 0.0005 mole) and dimethyl fumarate[62] (0.072 g., 0.0005 mole) in o-xylene (20 ml.), was refluxed for 4 hrs. The red colour which was produced at the initial stages of reflux, was discharged to leave a pale yellow solution. The solvent was removed in vacuo and the residual yellow oil was purified by chromatography on alumina, using benzene as eluent. After a yellow band was eluted (not further examined), the main fraction was collected (ca. 150 ml.). Evaporation of the solvent left a colourless oil which when triturated with hexane gave 4-acetyl-trans-2,3-dicarbomethoxy-2,3-dihydro-5-(cis-1,2-diphenylvinyl)furan(XXII) (0.080 g., 39.4%) as a white solid m.p. 141-142°. This product was purified by recrystallisation from ethanol m.p. 146.5-147°.

100 Mc. NMR spectrum: δ1.60 singlet (3H); δ3.64 singlet (3H); δ3.72 singlet (3H); δ3.72 doublet (1H) and 4.21 doublet (1H); δ7.26-7.82 multiplet (11H).

IR spectrum: $CHCl_3$ max 1730 cm^{-1} (C=O of an ester); shoulder at 1695 cm^{-1} (α,β-unsatd. C=O).

Mass spectrum: m/e 406,

Calcd. for $C_{24}H_{22}O_6$: 406.1416

Found: 406.1416

Anal. Calcd. for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46.

Found : C, 70.80; H, 5.38.

Reaction with N-Phenylmaleimide.

A solution of the 4-acetyl-4-oxazoline (0.263 g., 0.0005 mole) and N-phenylmaleimide[61] (0.087 g., 0.0005 mole) in o-xylene (20 ml.), was heated under reflux for 3 hr. The red colour produced initially upon reflux was slowly discharged to leave a yellow solution. The solvent was removed in vacuo and the residual yellow gum was purified by chromatography on basic alumina using benzene as eluent. A yellow band which was eluted first was evaporated free of benzene to leave a yellow oil which was not further examined. The second fraction (ca. 150 ml.), was evaporated free of benzene to leave a colourless oil. Trituration of this oil with hexane gave 3-acetyl-2-(cis-1,2-diphenylvinyl)-4,5-dihydrofurano-[4,5-c]-2',5'-dioxo-N-phenylpyrrolidine as a white solid (0.073 g., 33.5%), m.p. 207-209°. Recrystallisation from ethanol afforded the pure 2,3-dihydrofuran derivative (XIX) m.p. 215.5-216.5°.

NMR spectrum: δ 1.92 singlet (3H); AB quartet, centred at δ3.62, δ4.05, J=9Hz., (2H); δ6.70-8.00 multiplet (16H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1690 cm^{-1} (α,β-unsatd. C=O).
1715 cm^{-1} (imide C=O).

Mass spectrum: m/e 435,

Calcd. for $C_{28}H_{21}NO_4$: 435.1471.
Found: 435.1473.

Anal. Calcd. for $C_{28}H_{21}NO_4$: C, 77.23; H, 4.87; N, 3.22.
Found: C, 77.51; H, 5.03; N, 3.00.

4-Benzoyl-2-(p-biphenylyl)-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-oxazoline. (XIII)

Reaction with Diphenylcyclopropenone.

A solution of the 4-benzoyl-4-oxazoline (0.587 g., 0.001 mole) and diphenylcyclopropenone (0.206 g., 0.001 mole) in toluene (40 ml.), was heated under reflux for 12 hr. The deep red colour produced at first faded gradually to yield a yellow solution. The solvent was removed in vacuo and the residual gum was purified by chromatography on basic alumina using benzene as eluent. A yellow band was eluted first which after evaporation of the benzene and trituration of the residue with heptane gave 4-benzoyl-5-(cis-1,2-diphenylvinyl)-2,3-diphenylfuran (XVII) (0.448 g., 89.2%), as a yellow solid m.p. 192-193°. This material was identical in all respects (mixed m.p. and superposable IR spectrum) to that reported by Lown and Smalley (lit. m.p. 195-196°).[35]

Reaction with Dimethylfumarate.

A solution of the 4-benzoyl-4-oxazoline (0.587 g., 0.001 mole) and dimethylfumarate (0.144 g., 0.001 mole) in toluene (40 ml.) was heated under reflux for 12 hr., after which time the initial deep red colouration had faded to yield a pale yellow solution. Removal of the solvent *in vacuo* left a semi-solid residue which was triturated with heptane to yield 4-benzoyl-*trans*-2,3-dicarbomethoxy-2,3-dihydro-5-(*cis*-1,2-diphenylvinyl)furan (XVIII) (0.350 g., 74.7%), as a white solid m.p. 187-189° (red melt). This derivative was found to be identical in all respects (mixed m.p. and superposable IR spectrum) to that reported by Lown and co-workers.[36]

Reaction with N-Phenylmaleimide.

A solution of the 4-benzoyl-4-oxazoline (0.293 g., 0.0005 mole) and N-phenylmaleimide (0.087 g., 0.0005 mole) in toluene (20 ml.), was heated under reflux for 1½ hr. The solvent was evaporated *in vacuo* and the residual yellow oil was purified by chromatography on basic alumina using benzene as eluent. Compound 3-benzoyl-2-(*cis*-1,2-diphenylvinyl)-4,5-dihydrofurano-[4,5-c]-2',5'-dioxo-N-phenylpyrrolidine (XVI) was thus isolated as a white solid (0.212 g., 85.3%) m.p. 215-216°. Recrystallisation from ethanol afforded the pure product m.p. 222-223°, which was found to be identical in all respects (mixed m.p. and superposable IR spectrum) to that material reported by Lown, Smalley and Dallas.[23]

Acid Catalysed Preparation of Furan Derivatives.

It was found during the course of this work, that the reaction times involved in the preparation of furan derivatives of 4-oxazolines, could be reduced considerably by the addition of a minute trace of p-toluenesulfonic acid.

The reactions of 4-oxazolines with dipolarophiles could be completed in a matter of minutes in boiling benzene solution, using this modification, to give furans which corresponded to those described above. The yields of products were comparable to those given by thermal methods already described. An example is given.

4-Benzoyl-2,3-dicarboethoxy-5-(cis-1,2-diphenylvinyl) furan.

To a solution of 4-benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline (0.128 g., 0.00025 mole) in benzene (5 ml.), was added a minute trace of p-toluenesulfonic acid, whereupon the initial yellow solution assumed a pink-red colouration. Diethylacetylene dicarboxylate (0.050 g., 0.00029 mole) in benzene (1 ml.), was added immediately and the solution was boiled until the red colour was discharged to a yellow solution (10 min.). Chromatography on basic alumina, using benzene as eluent afforded the desired furan (0.057 g., 47%) m.p. 112°, identical in all respects to that material reported by Lown and Smalley.[35]

5. Chemical Dehydrogenation to Support the Proposed 2,3-Dihydropyrrole Structures.

These experiments were carried out with attention given to the work of Heine and Peavy, who describe chemical dehydrogenations of a similar nature to those about to be described here.[30]

5-(p-Biphenylyl)-2-carbomethoxy-1-cyclohexyl-3,4-diphenylpyrrole. (XI)

A solution of 5-(p-biphenylyl)-2-carbomethoxy-1-cyclohexyl-2,3-dihydro-3,4-diphenylpyrrole (0.170 g., 0.00033 mole) and p-chloranil (0.164 g., 0.00066 mole) in dry chlorobenzene (10 ml.), was heated under reflux for 24 hr. The resultant solution was cooled, diluted by addition of ether (25 ml.) and washed with (i) 4% sodium hydroxide solution (containing about 1% sodium bisulphite) (25 ml.), (ii) 2 x 25 ml. portions of water. The aqueous extracts were discarded, and the ethereal solution was dried ($MgSO_4$) and finally evaporated in vacuo to remove the solvents. The substituted pyrrole (XI) was thus obtained (0.132 g., 78.1%) as a tan solid m.p. 178-179°. The product was purified by recrystallisation from ethanol yielding the pure product as a white crystalline solid m.p. 186-186.5°.

NMR spectrum: δ0.9-2.4 multiplet (11H, cyclohexyl protons); δ3.53 singlet (3H, methyl protons of ester group); δ6.7-7.7 multiplet (19H, aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1698 cm^{-1} (α,β-unsatd. C=O).

Mass spectrum: m/e 511,

Calcd. for $C_{36}H_{33}NO_2$: 511.2511

Found: 511.2510

Anal. Calcd. for $C_{36}H_{33}NO_2$: N, 2.74.

Found: N, 2.92.

2-Carboisopropoxy-1-cyclohexyl-3,4,5-triphenylpyrrole. (XII)

A solution of 2-carboisopropoxy-1-cyclohexyl-2,3-dihydro-3,4,5-triphenylpyrrole (0.233 g., 0.0005 mole) and p-chloranil (2,3,5,6-tetrachloro-p-quinone) (0.123 g., 0.0005 mole) in dry chlorobenzene (13 ml.) was heated under reflux for 20 hr. The reaction mixture was then worked up exactly as described in the preceding experiment. The product (XII) after recrystallisation from ethanol was isolated as a white crystalline solid (0.180 g., 77.7%), m.p. 176°.

NMR spectrum: δ0.9 doublet J=6Hz. (6H, methyl protons of isopropyl group); δ0.77-2.46 multiplet (11H, cyclohexyl protons); δ4.0-5.17 multiplet (1H,-C-H proton of isopropyl group); δ6.6-7.4 multiplet (15H, aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1683 cm^{-1} (α,β-unsatd. C=O).

Mass spectrum: m/e 463.

Calcd. for $C_{32}H_{33}NO_2$: 463.2511

Found: 463.2512.

Anal. Calcd. for $C_{32}H_{33}NO_2$: C, 82.87; H, 7.18; N, 3.02.
Found: C, 83.13; H, 7.13; N, 3.21.

Reactions of (i) 2,3-dihydro-N-phenacylisoquinolinium bromide and (ii) N-Carbomethoxymethylene-2,3-dihydroisoquinolinium bromide with Diphenylcyclopropenone.

A number of attempts were made to effect reaction between these quaternary salts and diphenylcyclopropenone. No successfully identified product was isolated in any instance. A typical example is described as follows:-

Diphenylcyclopropenone (1.03 g., 0.005 mole) and 2,3-dihydro-N-phenacylisoquinolinium bromide (1.65 g., 0.005 mole) were stirred together in dry benzene (75 ml.). To this mixture a solution of triethylamine (2 ml.) in dry benzene (10 ml.) was added dropwise during 40 min. The resultant mixture was then stirred for 12 hr. and then filtered to remove the insoluble material. The filtrate was evaporated to dryness, the residue treated with dry ether and filtered to remove a further quantity of insoluble material. The ethereal solution was evaporated *in vacuo* and the residual red oil was purified by chromatography on basic alumina using chloroform as eluent. A yellow band was rapidly eluted which when evaporated to remove the chloroform left a red gum which was not successfully identified.

N-Phenacylpyridinium bromide was prepared according to the procedure described by Bamberger.[50]

Dimethylsulfoxonium phenacylide was prepared according to the method of Corey and Chaykovsky.[51]

Diphenylisobenzofuran was prepared according to the method of Newman.[52]

1-(N-pyrrolidino)-1-propene was prepared according to the procedure described by Opitz, Hellmann & Schubert. The product, a colourless oil (62%), was purified by distillation under reduced pressure b.p. 49-51°/19-20 mm. (lit., b.p. 38°/12 mm.).[53]

Monoperphthalic acid was prepared according to the procedure of Böhme.[54]

Triethyloxonium floroborate was prepared according to the method of Meerwein.[55]

N-Pyridiniumdibenzoyl methide was prepared according to the procedure described by Kröhnke.[56]

6. Reactions of Cycloheptenocyclopropenone with 4-Oxazolines.

4-Benzoyl-2,3-cyclohepteno-5-(cis-1,2-diphenylvinyl)-furan. (XXII)

A solution of cycloheptenocyclopropenone (0.061 g., 0.0005 mole) and 4-benzoyl-3-cyclohexyl-5-(cis-1,2-diphenyl-vinyl)-2-phenyl-4-oxazoline (0.256 g., 0.0005 mole) in toluene (10 ml.), was heated under reflux for 27 hr. The resultant pale yellow solution was distilled under reduced pressure to remove the solvent and the residual yellow oil was purified by chromatography on basic alumina using a 60:40 hexane: benzene mixture as eluent. A yellow band was rapidly eluted

which, after removal of the solvent and trituration under hexane, afforded the desired furan (XXII) as a yellow solid (0.067 g., 32%) m.p. 158°. The product was purified by recrystallisation from heptane yielding the pure furan derivative m.p. 160°.

NMR spectrum: δ 1.0-2.5 multiplet (10H, alicyclic protons); δ 6.73-8.03 multiplet (16H aromatic protons and vinyl proton).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1690 cm^{-1} (aromatic C=O).

Mass spectrum: m/e 418,

Calcd. for $C_{30}H_{26}O_2$: 418.1933

Found: 418.1935

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.12; H, 6.23

Found: C, 85.94; H, 6.32.

This furan derivative was also prepared by reaction of cycloheptenocyclopropenone with 4-benzoyl-2-(p-biphenylyl)-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-oxazoline by an identical procedure to that described above. The furan derivative was again isolated as a yellow crystalline solid (54.8%) m.p. 159°, identical in all respects (mixed m.p. and superposable IR spectrum) to that described previously.

With Stabilised Ylids.

3,4-Cyclohepteno-6-phenyl-2-pyrone. (XXIII)

Cycloheptenocyclopropenone (1.22 g., 0.01 mole) and N-phenacylpyridinium bromide (2.78 g., 0.01 mole) were dis-

solved in methanol (15 ml.). To this stirred solution was added by dropwise addition, a solution of N-ethyl-diisopropylamine (1.93 g., 0.015 mole) in methanol (10 ml.), during 45 min. After stirring for 24 hr., the mixture was filtered to remove the base hydrobromide which had separated and the filtrate was evaporated free of methanol and excess base to leave a dark brown tar. This residue was treated with benzene (50 ml.), and the benzene solution was decanted from an insoluble dark gum which was not further examined. The benzene solution was washed with (i) 2M. hydrochloric acid solution (50 ml.), (ii) water (50 ml.), then dried ($MgSO_4$). Evaporation of the solution followed by chromatography of the residual oil on basic alumina using benzene as eluent gave the desired 2-pyrone as a yellow oil. Trituration of this oil under heptane gave the desired product (XXIII) as a yellow solid (0.085 g., 3.6%) m.p. 112°. Purification was achieved by recrystallisation from heptane giving the pure product m.p. 114°.

NMR spectrum: δ1.15-2.18 multiplet (6H, alicyclic protons); δ2.46-3.0 multiplet (4H, alicyclic protons adjacent to carbon-carbon double bond); δ6.48 singlet (1H, 5-substituted vinylic proton); δ7.2-8.0 multiplet (5H, aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1690 cm^{-1} (α,β-unsatd. C=O).

Mass spectrum: m/e 240,

Calcd. for $C_{16}H_{16}O_2$: 240.1150

Found: 240.1139.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.01; H, 6.68

Found: C, 79.99; H, 6.81.

This 2-pyrone derivative could be prepared in better yield using dimethylsulfoxonium phenacylide according to the following procedure.

Cycloheptenocyclopropenone (0.61 g., 0.005 mole) and dimethylsulfoxonium phenacylide (1.0 g., 0.0051 mole) were dissolved in acetonitrile (15 ml.), and the solution was stirred for 24 hr. At the end of this period, the solution was heated under reflux for 2 hr., cooled and then evaporated in vacuo to remove the solvent. The yellow-brown residue was heated with benzene (25 ml.) and the hot benzene solution was decanted from a small quantity of dark brown insoluble material. Evaporation of the benzene, followed by chromatography on alumina using benzene as eluent gave the desired 2-pyrone derivative (XXIII) as a yellow crystalline solid (0.790 g., 65.8%), m.p. 114° (after recrystallisation). This product was identical (mixed m.p. and superposable IR spectrum) with that 2-pyrone derivative given by reaction with N-phenacylpyridinium bromide.

Reaction of Cycloheptenocyclopropenone with Diphenylisobenzofuran.

Two reactions were attempted, both without success. The first reaction was attempted in toluene at reflux for 24 hrs., using equimolar proportions of the reactants. Unchanged diphenylisobenzofuran was recovered unchanged (88.6%).

Cycloheptenocyclopropenone and diphenylisobenzofuran were heated together in o-xylene at reflux for 5 days, and again considerable quantities of starting materials were recovered and no product was isolated which would correspond to the material given by the analogous reaction with diphenylcyclopropenone.

Reaction of Cycloheptenocyclopropenone with an Enamine.

Cycloheptenocyclopropenone was treated with 1-(N-pyrrolidino)-1-propene according to the method and conditions used by Ciabattoni and Berchtold who have carried out similar work using diphenylcyclopropenone.[26] Other than tarry products which were not characterised, and a small quantity of unchanged enamine which was recovered, no significant product could be isolated from this reaction.

Reactions of Cycloheptenocyclopropenone with Aziridines.

Exactly similar conditions to those used in the case of diphenylcyclopropenone were used, but no successfully identified product has been isolated.

7. Reactions of Diphenylcyclopropenethione.

With 1-(N-pyrrolidino)-1-propene.

A solution of 1-(N-pyrrolidino)-1-propene (0.561 g., 0.0051 mole) in dry benzene (5 ml.), was added in one portion,

to a solution of diphenylcyclopropenethione (1.11 g., 0.005 mole) in benzene (10 ml.). An exothermic reaction ensued and crystals slowly separated from the resultant deep red solution. After standing for 1 hr., hexane (75 ml.) was added and the mixture was then filtered to yield 2,3-diphenyl-5-methyl-4-(N-pyrrolidino)-2-cyclopententhione (XXIV) (0.358 g., 21.5%), as a straw-coloured solid m.p. 179-180°. This product was purified by recrystallisation from benzene-hexane and finally from ethanol to yield the pure adduct m.p. 185°. The structure of the adduct was confirmed by spin-decoupling experiments in its proton resonance. Evaporation of the filtrate after removal of the product from the reaction mixture, afforded a dark red tar which was not further examined.

100 Mc. NMR spectrum: δ1.32 doublet (3H, methyl protons); δ1.86-2.51 multiplet (5H); δ2.92-3.42 multiplet (3H); δ4.4-5.0 multiplet (2H); δ6.83-8.0 multiplet (10H).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1030 cm^{-1}, 1070 cm^{-1} (C=S).

Mass spectrum: m/e 333,

Calcd. for $C_{22}H_{23}NS$: 333.1552

Found: 333.1548

Anal. Calcd. for $C_{22}H_{23}NS$: C, 79.23; H, 6.95; N, 4.20.

Found: C, 79.05; H, 6.96; N, 4.33.

With 4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-oxazoline.

A number of experiments were performed attempting to react diphenylcyclopropenethione with a substituted 4-oxazoline. The procedures used were analogous to those previously described for diphenylcyclopropenone. No successfully identified products could be isolated.

Oxidation of Diphenylcyclopropenethione in Attempts to Prepare the S-Oxide Derivative.

Using Lead Tetraacetate.

The method used is based on a procedure used by Adley, Anisuzzaman and Owen for the oxidation of thiocarbonates.[42]

To a solution diphenylcyclopropenethione (1.11 g., 0.005 mole) in acetic acid (285 ml.), was added over 12 min., with stirring, a solution of lead tetraacetate (4.5 g., 0.01 mole) in acetic acid (190 ml.). The solvent was removed by distillation under reduced pressure and the residue was shaken with water (20 ml.). Chloroform (20 ml.) was added and the mixture was filtered to remove the black lead oxide which had deposited. The aqueous layer was discarded and the chloroform solution was dried ($MgSO_4$) and evaporated to yield a red gummy residue. This residual gum was dissolved in the minimum volume of hot cyclohexane and when the solution was allowed the cool, yellow crystals were deposited m.p. 115-119°. This product was further purified by recrystallisation from cyclohexane to yield a white crystalline solid (0.22 g.,

21.4%) m.p. 120°. This product was characterised unambiguously (mixed m.p. and superposable IR spectrum) as diphenylcyclopropenone.

Using m-Chloroperbenzoic acid.

To a solution of diphenylcyclopropenethione (1.11 g., 0.005 mole) in methylene dichloride (20 ml.), was added over 10 min., with stirring, a solution of m-chloroperbenzoic acid (0.90 g., 0.0052 mole) in methylene dichloride (15 ml.). The mixture was stirred for 1½ hr. and then washed with a solution of sodium bicarbonate (1.5 g.) in water (50 ml.). The aqueous washings were discarded and after drying the methylene dichloride solution ($MgSO_4$), the solvent was evaporated to leave a red gummy residue. This residue was treated with hot cyclohexane (15 ml.), and a quantity of a yellow solid was isolated from the hot solution by filtration. This insoluble material (m.p. 119°), was readily identified and characterised as elemental sulfur. The filtrate upon cooling deposited diphenylcyclopropenone (0.550 g., 53%), as a white solid m.p. 115-117°, identified by comparison with an authentic sample.

Using Monoperphthalic Acid.

This oxidant was used with reference to the work of Strating and co-workers, who oxidised fluorene-9-thione to its corresponding S-oxide with monoperphthalic acid.[57]

A considerable number of experiments were attempted using monoperphthalic acid, before the optimum conditions were realised. The unsuccessful attempts were largely due

to the thermal instability of diphenylcyclopropenethione-S-oxide.

Diphenylcyclopropenethione (1.11 g., 0.005 mole) was dissolved in methylene chloride (50 ml.) and the resultant solution was cooled to -40°. To this solution, was added dropwise over 10 min., with stirring, a solution of monoperphthalic acid (0.985 g., 0.0054 mole) in ether (20 ml.), the temperature being maintained below -30°. Stirring was continued for 10 min., after the addition had been completed, and the yellow solid which had slowly separated during the addition was filtered, ground into fine particles, and added in one portion to a stirred solution of 4% sodium bicarbonate (50 ml.), the temperature being maintained at 5°. At this stage, a reaction ensued with the liberation of carbon dioxide and diphenylcyclopropenethione-S-oxide was deposited as a bright orange solid (0.80 g., 67.2%) m.p. 40° (dec.). The product was collected by filtration into a previously cooled apparatus and washed through the filter with iced water. It was stored and dried in a cooled, evacuated desiccator which contained pellets of sodium hydroxide. Further purification was found not to be possible due to the instability of this product.

100 McNMR spectrum: δ 7.0-8.3 (aromatic protons).

IR spectrum: $\nu_{max}^{CHCl_3}$ 1068 cm^{-1}, (C=S=O).[57]

1350 cm^{-1}, (C=S).

Visible spectrum: Shoulder 420 mμ. λmax 325 mμ.

Anal. Calcd. for $C_{15}H_{10}SO$: C, 75.60; H, 4.23; S, 13.43

Found: C, 73.16; H, 4.42; S, 12.28.

Calcd. $\frac{C}{S}$ = 5.63 Found: $\frac{C}{S}$ = 5.96.

Controlled Decomposition of Diphenylcyclopropene-thione-S-oxide.

The S-oxide was prepared exactly as described previously and decomposed by steam distillation. Hydrogen sulfide and sulfur dioxide were recognised as decomposition products by their smell and by their reactions with lead acetate and potassium dichromate papers respectively. When no more steam-volatile material distilled, the steam distillate (250 ml.) was extracted with ether, the ether extract dried ($MgSO_4$) and evaporated to yield an off-white crystalline solid. This material was unambiguously identified as diphenylacetylene (0.083 g., 9.4%) m.p. 60°, by comparison with an authentic sample (mixed m.p. and superposable IR spectrum). In the distillation flask there remained a quantity of a green solid, presumably polymeric in nature, but this was not further investigated.

Preparation of the Meerwein's Salt Derivative of Diphenylcyclopropenethione.

This experiment was carried out with close reference to the work of Breslow and co-workers who have prepared the corresponding derivative of diphenylcyclopropenone.[7]

A solution of diphenylcyclopropenethione (0.65 g., 0.0029 mole) and triethyloxonium fluoroborate (1.2 g., 0.0055 mole) in dry methylene chloride (4.5 ml.) was allowed to stand for 1 hr. Anhydrous ether (10 ml.) was added and the pasty precipitate which resulted was triturated until completely solid. The derivative was filtered, washed through the filter with anhydrous ether followed by a small quantity of anhydrous ethanol, affording the desired adduct as a tan solid (0.74 g., 75.5%) m.p. 165-166°.

Anal. Calcd. for $C_{17}H_{15}BF_4S$: C, 60.35; H, 4.44.

Found: C, 58.62; H, 4.54.

A similar experiment carried out with diphenylcyclopropenethione-S-oxide was unsuccessful as no satisfactory adduct could be isolated.

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